ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР
ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК

BULLETIN OF THE ACADEMY OF SCIENCES

OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMY NAUK SSSR)

(OTDELENIE KHIMICHESKIKH)

IN ENGLISH TRANSLATION

1957 NO. 12

CONSULTANTS BUREAU, INC.

227 WEST 17TH STREET, NEW YORK 11, N. Y.

an agency for the interpretation of international knowledge

What are the Russians doing in my particular field? . . .

Is this information available in translation?

These pertinent questions which consistently confront technical librarians today, have pointed up the serious lack of a *standard source of reference* for translations of Soviet scientific information, and have led to the inauguration of a unique monthly service. . . .

Soviet Science and Technology

THIS HANDY MONTHLY GUIDE, available on an annual subscription basis, is specifically designed to furnish Western scientists with *English translations of the contents* of current Soviet journals being translated, cover to cover, on a *continuing basis* by Consultants Bureau, other firms and learned societies.

THROUGH SPECIAL ARRANGEMENT with the editors of these Soviet publications, expedited copies of the contents are made available, in translation, within two months after their release in Russia. Thus, each subscriber is constantly aware of the latest information available for translation in his specific field of scientific endeavor.

The format of SST is one which permits the reader instant access to all pertinent information:

a) *Estimated date of publication in English* (when information is available from publisher)

b) *Name and address of organization from which translation is available*

c) *Yearly subscription prices*

d) *Price of individual papers, or issues* (when sold separately)

e) *A special section devoted exclusively to editorial material on the most up-to-date translating techniques*

The worldwide acceptance of SST in its few short months of existence (*first issue published in May, 1958*), has proved the urgent need for just such a service. And with the constant addition of *new* Russian journals-in-translation, each subscriber is assured of continuous, comprehensive and accurate information on the availability of the latest advances in SOVIET SCIENCE AND TECHNOLOGY.

ANNUAL SUBSCRIPTION

(includes 12 issues per year, which cover all calendar year issues of the original Russian journals)

1 copy	$25.00 per copy
10-100 copies	18.00 per copy
100-500 copies	15.00 per copy
500 copies and over	11.50 per copy

(500 copies includes, free of charge, your own special organizational cover)

AVAILABLE FOR A LIMITED TIME

One volume containing the contents for all 1957 issues of these journals, with the same information as in the 1958 SST. . . . $15.00

Write Consultants Bureau for free brochure on SST, and comprehensive catalogs of our current Russian translation-publishing program.

C/b CONSULTANTS BUREAU, INC.
227 W. 17th St., NEW YORK 11, N.Y.

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR DIVISION OF CHEMICAL SCIENCES

(IZVESTIYA AKADEMII NAUK SSSR
OTDELENIE KHIMICHESKIKH NAUK)

1957, No. 12

December

Editorial Board

M. M. Dubinin (Editor), A. F. Kapustinsky (Asst. Editor), V. N. Kondratyev,
A. N. Nesmeyanov, K. T. Poroshin (Secretary), I. I. Chernyaev

---

IN ENGLISH TRANSLATION

Copyright, 1958

CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, N.Y.

Printed in the United States

	Domestic	Foreign
Annual Subscription	$45.00	$50.00
Annual Subscription for libraries of non-profit academic institutions	15.00	20.00
Single Issue	5.00	

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

NEW DATA ON THE CHEMISTRY OF SOME OF THE RARE ELEMENTS

I.V. Tananaev

(Paper read at a session of the Division of Chemical Sciences of the Academy of Sciences of the USSR, October 31, 1957)

In recent years the study of rare and widely scattered elements and their compounds has been intensified, which is to be explained by their greatly increased importance in technology. There has therefore been a great increase in the amount of research devoted to the properties of rare elements and the preparation of new compounds of these elements. It is understandable, therefore, why such interest is taken in individual results on the chemistry of rare elements and why such efforts are made to generalize these results. We here report some new data on the chemistry of rare elements; these have some theoretical importance and can be applied in practice in the development of new methods of extracting rare elements from natural raw materials and obtaining them in a pure state, in the development of methods of determining them analytically, and so on. It is important to note that these data were usually obtained by an extensive use of the methods of physicochemical analysis, but in a nontraditional form applied to nontraditional processes, so that the procedures required had to be worked out. This applies, in particular, to solubility and spectrophotometry methods. A new method was proposed for use in the study of heterogeneous systems: the measurement of the apparent volumes of precipitates.

The investigation of these systems demanded their parallel study by different methods. Thus, when this was possible the systems were studied by the following methods: solubility, conductivity, spectrophotometry, emf measurements, and the measurement of volumes of precipitates. Such a "combined" approach to the investigation of the systems enabled us to characterize individual processes and compounds, etc., as thoroughly as possible, so that the resulting data were as reliable as possible. This approach to the study of chemical reactions was developed over a period of years in the Laboratory for the Chemistry and Analysis of Rare Elements at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR and has been generally adopted in that laboratory.

One of the most urgent problems consists in the development of new reactions for the detection, determination, and separation of the rare alkali metals, lithium, rubidium, and cesium.

As experience over many years in the study of the composition and properties of ferrocyanides of various metals has shown, they almost all form practically insoluble mixed ferrocyanides with alkali metals. Table 1 gives the compositions of mixed ferrocyanides of "heavy" metals (E) with alkali metals and univalent thallium (M). The table gives only those data which were obtained by physicochemical analysis of systems in which the mixed ferrocyanides listed are formed; data obtained by other investigators by the preparative method are not given, as being less trustworthy. It will be seen that the class of insoluble mixed ferrocyanides is very extensive, and there is great variation in composition. The possibility of a wide choice of reagents for the alkali metals is presented.

It should be noted that by no means every heavy-metal ferrocyanide can be used as a specific reagent for a given alkali metal, just as it is not possible in all systems to establish conditions that will ensure the desired selectivity of precipitation. However, on the basis of the fact that in any given ferrocyanide system, alkali metals fall in the following series with respect to their tendency to pass into the precipitate:

$$Cs (= Tl) > Rb > K > Na > Li,$$

TABLE 1

Types of Mixed Ferrocyanides (M and E denote alkali and "heavy" metals, respectively; R = $[Fe(CN)_6]$)

E	Mixed ferrocyanides	M	E	Mixed ferrocyanides	M
Li	M_3ER	Cs	Cu	$M_2E_3R_2$	K
Ag	ME_3R	K, Rb, Cs, Tl		$M_4E_4R_3$	Rb
	M_2E_2R	Rb, Cs, Tl		M_2ER	Cs
	M_3ER	Cs, Tl	Mn	M_2ER	Na, K
Mg	$M_4E_4R_3$	Cs	Zn	$M_2E_3R_2$	K
	$M_{10}E_7R_6$	Tl	Cd	$M_{16}E_{10}R_9$	K
	$M_{12}E_8R_7$	Rb, Cs	Co	$M_4E_{20}R_{11}$	Na
	M_2ER	Rb, Cs, Tl		$M_4E_{10}R_6$	K
Ca	M_2ER	K, Rb, Cs, Tl		$M_2E_3R_2$	Cs
Sr	M_2ER	Cs		$M_{12}E_8R_7$	K
Y	$M_4E_8R_7$	K		M_2ER	Cs
	MER	Rb, Cs	Ni	$M_2E_3R_2$	Na, Tl
La	MER	Li, Na, K, Rb, Cs, Tl		$M_4E_4R_3$	K, Tl
Ce	$M_4E_8R_7$	Na	Fe	MER	K, Rb, Cs
	MER	K, Rb, Cs, Tl		$M_6E_2R_3$	K, Rb, Cs
Pr, Nd	MER	Na, K, Rb, Cs		M_5ER_2	K
Sm	MER	Na, K, Rb, Cs		$M_{14}E_2R_5$	Rb
Ga	MER	Na, K		M_9ER_3	Cs
In	MER	K, Rb, Cs	UO_2	$M_2E_3R_2$	K, Rb, Cs, Tl
	$M_7E_3R_4$	Cs		$M_4E_4R_3$	K, Rb, Cs, Tl

it is possible to realize, in some measure, the fractional precipitation of alkali metals. The mixed ferrocyanide functions here as a sort of peculiar ion-exchange agent, so that the procedure in the separation of alkali metals can be based, in this case, on the principle of column chromatography. Thus, the precipitation of cesium and rubidium in presence of large amounts of potassium can be carried out fairly readily with the aid of ferrocyanides of many nonalkali metals, including magnesium, calcium, cobalt, and nickel. Cesium and rubidium can be largely separated with the aid of strontium ferrocyanide. The quantitative determination of potassium in presence of sodium and lithium is readily performed with the aid of a system of Cd^{2+} and $[Fe(CN)_6]^{4-}$ ions.

However, the practical question of the conditions required for the quantitative precipitation of lithium as a mixed ferrocyanide has still not been solved. As will be seen from Table 1, a system of La^{3+} and $[Fe(CN)_6]^{4-}$ ions forms the only means of precipitating lithium; with the remaining metals lithium does not form insoluble mixed ferrocyanides, if we pass over the rather unstable mixed ferrocyanides of lithium with copper and nickel, which are precipitated in presence of excess of $Li_4[Fe(CN)_6]$ and are, of course, not of interest. It would not be an exaggeration, however, to state that further study of mixed ferrocyanides will enable us to find convenient procedures for the separation of all the alkali metals, including lithium. The use of ferrocyanides for this purpose is favored by the fact that mixed ferrocyanides are generally of extremely low solubility. Thus, there is no particular difficulty in precipitating 0.0002 g of rubidium (or one hundredth of this amount of cesium) almost quantitatively from 1000 ml of solution.

Lithium, rubidium, and cesium fluorides should acquire some importance particularly in the search for the most convenient methods of preparing specially pure liquid hydrogen fluoride and fluorine. Thus, a comparison of potassium hydrogen fluoride as a source of liquid hydrogen fluoride with the highly acid sodium fluorides which we have isolated for the first time (NaF · 2HF, NaF · 3HF and NaF · 4HF) and with LiF · HF shows that the latter have considerable advantages, particularly LiF · HF. It is not a question only of greater readiness to give up hydrogen fluoride (which, in the case of LiF · HF, proceeds even at room temperature) and the more convenient, free-flowing residue left after removal of hydrogen fluoride, but also of the very low solubility of LiF · HF. Thus, by the action of 40% HF solution on almost insoluble LiF we may obtain the very sparingly soluble LiF · HF, from which HF can be driven off at a low temperature; consequently, it is much easier to find a suitable material for the construction of the apparatus. We may add that the usual contamination with silicon, generally precipitated in the form of sparingly soluble $K_2[SiF_6]$ and $Na_2[SiF_6]$, does not occur with LiF · HF owing to the very high solubility of $Li_2[SiF_6]$.

On the basis of the difference in dissociation pressure between NaF · HF and LiF · HF we have proposed a method for the determination of small amounts of sodium in metallic lithium (when a mixture of these two salts is heated at 100°, the residue consists of LiF and NaF · HF, which can be titrated with alkali). By making use of the high solubility of $Li_2[SiF_6]$ and the almost complete insolubility of $Na_2[SiF_6]$ in 60-70% alcohol solution, we were able to determine lithium and sodium separately in a mixture, alkali being used as titrant.

It is known that the acid fluorides of rubidium and cesium have very low melting points: RbF · 2HF melts at 51.7° and CsF · 2HF at 19°. This fact can be applied to economic advantage in the electrolytic preparation of fluorine. In view of the possibility of obtaining large amounts of rubidium in our country, this question should attract attention.

In recent years there has been increased interest in the preparation of anhydrous LiG*, which is a useful material for scintillation counters. The preparation of satisfactory material is far from simple. By the method of vacuum sublimation, a pure material free from even traces of water has been obtained.

Many papers have been published in recent years on the chemistry of rare-earth metals: these seem to indicate that there has been a marked change in the situation regarding their preparation, particularly in the pure state. The great majority of investigations in this field have been devoted to the search for reagents that facilitate the chromatographical separation of rare-earth metals and to the determination of the efficiencies of these processes. Less attention has been given to the synthesis of new compounds of the rare-earth metals and to the study of their structures and their reactivities. However, systematic work in this direction is extremely necessary, for, apart from theoretical information that will enrich our knowledge of this field, which suffers from a lack of factual material, new possibilities may be revealed for the separation of rare-earth metals based, for example, on suitably selected reactions of fractional precipitation.

As experiment shows, differences in the chemical properties of rare-earth metals are greater than they seem to be at first glance. By way of example we may cite data on the composition of rare-earth ferrocyanides. The older literature shows that, when precipitated with $K_4[Fe(CN)_6]$ all rare-earth metals give precipitates of the general composition $KE[Fe(CN)_6]$. However, for precipitation with ferrocyanides of other alkali metals the picture may be different. Table 2 gives the compositions of mixed ferrocyanides of some rare-earth metals precipitated from their salts with M_4R (M = Li, Na, K, Rb, Cs, Tl; R = $[Fe(CN)_6]$). It follows from these data that the predominant form of the mixed ferrocyanide is MER. Here we can speak only of a regular reduction in the

*As in original – Publisher's note.

solubility of the mixed ferrocyanides with increase in the atomic weight of the alkali metal and also, in the series Ce–Sm, with increase in the atomic weight of the rare-earth metal. Nevertheless, an appreciable difference is observed between individual rare-earth metals, which is expressed in a change in coordination number. If we imagine that these compounds have structures of the type $M_n[E[R]]$, i.e., if we assume a differentiated "internal sphere" in the mixed ferrocyanide, then we observe a change in the strength of the bond in the compounds with sodium. Thus, whereas with cerium only the lower form of mixed salt $Na_4Ce_3R_7$ is found, with praseodymium and neodymium the normal form NaER is formed, though it is still incongruently soluble; with samarium it is again normal, but is now congruently soluble. The question now arises of how the type and solubility of mixed ferrocyanides will vary in the yttrium group. If the same tendency is shown here as in the series Ce–Sm, then the forms given by yttrium (which is characterized by the absence under the same conditions of an insoluble mixed ferrocyanide with sodium and the formation of only the lower form $K_4Y_3R_7$ with potassium) cannot be regarded as typical of the group.

Hence, in the search for chemical differences among the rare-earth metals it is necessary to select criteria more carefully in characterizing individual reagents. When we take the ferrocyanides of potassium and, particularly, rubidium, cesium and univalent thallium as our reagents, then with respect to these the chemical properties of the rare-earth metals are leveled out if the criterion is the type of mixed salt formed. On the other hand, as Table 2 shows, fairly substantial differences are to be observed in the interaction of rare-earth compounds with lithium and sodium ferrocyanides. Incidentally, it is with these same reagents that the greatest difference is found in the behavior of yttrium, which can be separated from elements of the cerium group on this basis.

TABLE 2

Compositions of Mixed Ferrocyanides of Rare-Earth and Alkali Metals (M denotes alkali metal; R denotes $[Fe(CN)_6]$)

M_4R	Rare-earth metal				
	La	Ce	Pr and Nd	Sm	Y
Li_4R	LiLaR	Ce_4R_3	E_4R_3	Sm_4R_3	No precipitate is formed
Na_4R	NaLaR	$Na_4Ce_3R_7$	NaER*	NaSmR**	
K_4R	KLaR	KCeR	KER	KSmR	$K_4Y_3R_7$
Rb_4R	RbLaR	RbCeR	RbER	RbSmR	RbYR
Cs_4R	CsLaR	CsCeR	CsER	CsSmR	CsYR
Tl_4R	TlLaR	TlCeR	—	—	—

*Incongruently soluble.

**Congruently soluble.

In conclusion, the quite exceptional behavior of lanthanum should be noted: no simple ferrocyanide of this element has been obtained, even by the use of $Li_4[Fe(CN)_6]$, $Na_4[Fe(CN)_6]$, $H_4[Fe(CN)_6]$ and $Ca_2[Fe(CN)_6]$. Moreover, the mixed lanthanum ferrocyanides given in Table 2 are much less soluble than others of this type. Lanthanum is anomalous in its behavior toward lithium ferrocyanide, similar phenomena not being observed with any other metal examined. The only explanation that has been found for this anomaly in the series of rare-earth metals is the absence of 4f electrons in the lanthanum atom.

In the chemistry of rare-earth metals an important part is played by soluble complexes of their compounds, which are used in the fractional precipitation of these metals and in their chromatographic separation. Possible complex-formers include salts of tartaric, citric, and ethylenedinitrilotetraacetic acids. Although considerable attention has been paid to the practical side of the question, mainly to the choice of optimum conditions for elution, hardly any investigation of complex formation with the aid of physicochemical analysis has been carried out.

Solubility studies on the systems $Sm(NO_3)_3-C_4H_6O_6-H_2O$ and $Sm(NO_3)_3-Na_2C_4H_4O_6-H_2O$ showed that in

the first system, which contains tartaric acid, normal samarium tartrate is formed and there is no complex formation, whereas in the second, which contains sodium tartrate, quantitative precipitation of samarium tartrate (solubility product $1 \cdot 10^{-16}$) first occurs, and this is then dissolved in excess of reagent with formation of the soluble complex ion $[Sm(C_4H_4O_6)_2]^-$, the instability constant of which was found to be $2.42 \cdot 10^{-7}$.

Investigation of the reaction of samarium ions ($Sm(NO_3)_3$) with di- and tetra-sodium salts of ethylenedinitrilotetraacetic acid showed that the complex ions $[Sm(H_2Y)_2]^-$ and $[SmY]^-$ are formed in solution. The compositions of complex compounds of this type therefore undergo considerable changes, depending on the pH of the medium. There can be no doubt that more extensive application of physicochemical analysis to suitable systems can provide new data, which would make it possible to rationalize the separation of rare-earth metals with the aid of complex formation.

These considerations apply even to such simple rare-earth compounds as the hydroxides. In spite of the great importance of the precipitation of hydroxides in the treatment of rare-earth raw materials, hardly any attention has yet been paid to the study of the dependence of the composition of the precipitate on the relative amount of alkali used. The important point here is that even the rare-earth elements of the cerium group, which are hydrolyzed relatively slightly in solution, form basic salts, which do not react very readily with alkali with formation of normal hydroxides.

By way of example we may cite the precipitation of neodymium. With $Nd_2(SO_4)_3$ reaction proceeds in two stages with formation of $Nd_2(OH)_4SO_4$ and $Nd(OH)_3$ successively. With $Nd(NO_3)_3$, $Nd_2(OH)_5NO_3$ and $Nd(OH)_3$ are formed. The stability of the basic salt generally depends on the anion present: in this case the basic sulfate is much more stable than the basic nitrate.

From these examples it will be clear that the solubility products given in the literature for rare-earth hydroxides, which are calculated from pH data etc., must be treated with great caution. Account must be taken also of the fact that the tendency of rare-earth metals to form basic salts increases with increase in atomic number.

There is still not enough material in the literature on the chemical properties of widely scattered elements, in particular gallium, indium, and germanium, so that the further study of compounds of these elements is of considerable interest. Until recently no details were known of the chemistry of the reaction of gallium and indium ions with alkalis. Physicochemical analysis of suitable systems showed that, whereas aluminum and gallium behave very similarly in such systems (formation first of a soluble salt and then of insoluble basic salts, conversion of the latter into the normal hydroxide, and solution of this in excess of alkali), indium forms basic salts and then the normal hydroxide, which does not dissolve in excess of alkali. It was found that existing views on the amphoteric properties of indium hydroxide were greatly exaggerated. Investigation of the solubility of $In(OH)_3$ in NaOH solutions (up to very high concentrations) showed that the formation of indates proceeded to a quite insignificant extent (the indate concentration was about 10^{-3} mole/liter). It is therefore possible to separate elements having alkali-soluble hydroxides (zinc, aluminum, chromium, etc.) from indium.

It is important to note that the great difference in chemical properties between gallium and indium is shown also in some other compounds. Thus, the double sodium gallium fluoride has the formula $13NaF \cdot 5GaF_3$, whereas for aluminum we have $11NaF \cdot 4AlF_3$ and indium forms $3NaF \cdot InF_3$. Both double salts are very sparingly soluble in solutions containing excess of precipitant (NaF), so that it is possible to effect the quantitative separation of gallium and indium from many other metals which have soluble fluorides.

A comparative study of the stepwise process of complex formation in the reaction of gallium and indium ions with fluoride ions in solution gave interesting results. As in the case of aluminum, gallium gives complex ions GaF_2^+ which do not readily dissociate and have an instability constant of $1.4 \cdot 10^{-9}$; on the other hand, under the same conditions indium forms considerably less stable InF_2^+ ions which have an instability constant of $1.9 \cdot 10^{-7}$. A similar picture is observed also in the reaction of gallium and indium with tartrate and citrate ions at various pH values. Whereas the presence of $GaC_4H_4O_6^+$ and $[Ga(C_4H_4O_6)_2]^-$ ions in solution is quite clearly established by composition-property diagrams, the identification of the corresponding compounds of indium in this way is much less clear. It was proved that indium ions have a much lower tendency to replace hydrogen in the OH groups of hydroxy acids. Also, indium tartrate (basic salt) is of low solubility. There is also a considerable difference between the two metals in behavior toward oxalate ions. For gallium it has been established that the stable ions $Ga_2(C_2O_4)_3$, $[Ga(C_2O_4)_2]^-$ and $[Ga(C_2O_4)_3]^{3-}$ are formed in solution; indium, however, gives the precipitate $In(OH)C_2O_4$, which is soluble in excess of oxalate with formation of $[In(C_2O_4)_2]^-$.

The existing physicochemical data show that in most cases gallium is a more powerful complex-former than indium, and also than aluminum, which is in accord with the values of their atomic radii. This is illustrated particularly clearly by the tendency for replacement of hydrogen in the hydroxy group of hydroxy acids (reaction with sodium tartrate), which is very marked in gallium, less marked in aluminum, and still less marked in indium. On the other hand, indium forms much less soluble simple and mixed ferrocyanides (the only ferrocyanide that is still less soluble is that of silver). New volumetric and colorimetric methods of determining indium in presence of many other metals have been based on this fact.

There is considerable interest in the Group IV rare elements zirconium and germanium. The properties of their compounds are being carefully studied at the present time, this work being prompted in the first case by the search for the best methods of separating zirconium from hafnium, and in the second case by the search for economic methods of extracting germanium from various natural sources. In both cases attention is directed mainly to various complex-formation reactions, which is of some interest in view of certain peculiarities in the behavior in solution of quadrivalent metal ions, which, owing to their great tendency to undergo hydrolysis, require an acid medium. This can be seen particularly clearly from the behavior of zirconium salts toward ferrocyanide ions. This reaction is used for the separation of hafnium from zirconium, but the composition of the precipitate formed has not yet been established. It is known that almost all metals form not only normal, but also mixed ferrocyanides with alkali metals. Investigation of the reaction of $ZrOCl_2$ with $M_4[Fe(CN)_6]$ (M = Li, Na, K, Rb, Cs) showed that the basic salts $[ZrO(OH)]_4[Fe(CN)_6]$ and $(ZrO)_2[Fe(CN)_6] \cdot Zr(OH)_4$ are precipitated even when the solution contains as much as 0.1 mole/liter of free HCl. Increase in acidity (HCl) up to 3-4 moles/liter results in the precipitation of the normal ferrocyanide $Zr[Fe(CN)_6]$. However, even at this acidity, mixed ferrocyanides are not formed, even when precipitation is carried out in presence of rubidium ions. This marked difference between zirconium and other metals is evidently to be explained by the fact that, owing to its quadrivalent condition, all of its valences are fixed in the formation of the ferrocyanide, and this prevents the formation of chainlike structures characteristic of metals of lower valence, particularly bivalent metals.

It is interesting that the ferrocyanides of zirconium differ from the fluorides with respect to the tendency for high coordination numbers to be found. It must be stated, however, that it is very difficult to obtain complex zirconium fluorides containing more than three KF molecules from aqueous solutions. Thus, in the investigation of solubility in the system ZrF_4-KF-H_2O, compounds such as $4KF \cdot ZrF_4$ and $5KF \cdot ZrF_4$ were not isolated. On the other hand, replacement of oxygen in the ZrO^{2+} ion by fluorine proceeds very readily, e.g., by reaction of $ZrOCl_2$ with dilute HF solutions. Investigation of this system by conductivity and pH methods showed that the $[ZrF_6]^{2-}$ ion is formed when the stoichiometric ratio $HF : ZrOCl_2 = 6$. This emphasizes the high strength of the zirconium-fluorine bond. Many other ions differ greatly from fluoride ions in reactivity toward ZrO^{2+} ions. Thus, addition of salts such as Na_2SO_4 and $Na_2C_2O_4$ to a solution of $ZrOCl_2$ does not produce an alkaline reaction to phenolphthalein, as in the case of addition of KF. Nevertheless, the behavior of zirconium in solution is greatly dependent on the anion. Thus, in the passage of $ZrOCl_2$ and $Zr(SO_4)_2$ solutions through an ion-exchange column, quite different absorptions of zirconium by the cation-exchange resin were observed.

It is interesting to compare the properties of the systems ZrO_2-HF-H_2O and GeO_2-HF-H_2O. In both cases trihydrates of the type $MF_4 \cdot 3H_2O$ (more correctly regarded as $H_2[MOF_4] \cdot 2H_2O$) and hydrates of free hexafluo acids, $H_2[ZrF_6] \cdot 2H_2O$ and $H_2[GeF_6] \cdot 3H_2O$ were isolated. The fluogermanate could be isolated only at very low temperature owing to the extremely high solubility of the acid (a solution saturated at 25° is very close in composition to the melt of $H_2[GeF_6] \cdot 3H_2O$). Neither acid has been previously isolated in the free state.

Various hexafluogermanates (cobalt, nickel, magnesium, ferrous, and others) were isolated. Investigations of their crystal structures showed that all six fluorine atoms are attached to germanium in the form of the complex ion $[GeF_6]^{2-}$, as in the case of the complex anion $[PtCl_6]^{2-}$.

There are references in the literature to the ability of germanium to form complexes with oxalate ions, but the corresponding free acid has not been isolated. By a careful investigation of solubility relations in the system $GeO_2-H_2C_2O_4-H_2O$, we succeeded in isolating solid $H_2[Ge(C_2O_4)_3] \cdot 6H_2O$ in the pure state and in obtaining several of its salts with bivalent cations.

To conclude this short review we must emphasize that the investigation of the chemistry of rare elements and the provision of new experimental data on the compositions and reactivities of their compounds constitute an important task, and the extension of work in this direction is of great importance for modern technology.

SUMMARY

New data are presented concerning the compositions and physicochemical properties of various compounds of some rare elements. The insoluble mixed ferrocyanides formed by various metals with lithium, rubidium, and cesium are reviewed, and new precipitating reagents for these elements are recommended. Regularities to be observed in changes in the compositions of mixed ferrocyanides of rare-earth metals are pointed out. Data are given on the compositions and stabilities of fluorides, oxalates, tartrates, and other compounds of gallium, indium, zirconium, and germanium.

Received October 9, 1957

N.S.Kurnakov Institute of General and
Inorganic Chemistry
Academy of Sciences, USSR

SOME GENERAL QUESTIONS OF ELECTROCHEMICAL KINETICS AND THE THEORY OF IONIC REACTIONS

A.N. Frumkin

(Paper read at a session of the Division of Chemical Sciences of the Academy of Sciences of the USSR, October 31, 1957)

In the evolution of modern electrochemistry we can distinguish three stages, each of which has exerted and still continues to exert an influence on chemistry as a whole. I shall refer only briefly to the first two, since their significance is generally known. The experimental investigation of the laws underlying the conductivity of salts and acids led to the inference of the existence of free ions in solutions, and this view was then developed in a brilliant manner as a result of x-ray investigation of the structure of salt crystals. Establishment of the relation between the free energy of formation of chemical compounds and the emf of reversible cells resulted in the development of a very effective method of investigating the state of solutions with the aid of measurements of equilibrium potentials, and the application of this method is constantly expanding.

The third stage in the history of electrochemistry, which began about a quarter of a century ago, is characterized by the development of electrochemical kinetics. As a prerequisite to this development it was necessary to make a more profound study of the structure of the metal-electrolyte interface by the use of several new physical methods of investigation. In this paper I should like to show with the aid of some examples with which I have been closely concerned that the development of this side of electrochemistry again enables us to establish some close relations with adjacent fields of physical chemistry. The results obtained up to now are still modest in significance and cannot be compared with those referred to above, but I consider that they are of definite scientific interest.

1. Adsorption of Gases on the Surface of Solid Metals

Calculation of the rate of a heterogeneous chemical process as a function of the pressures of the gases taking part in the reaction requires a knowledge of their adsorption isotherms with respect to the catalyst surface. In the early stages of the evolution of the theory of heterogeneous catalysis, the Langmuir isotherm was generally used for this purpose. The determination of charging curves, i.e., the measurement of the relation between the potential of an electrode and the amount of electricity passed under conditions such that this electricity is used entirely for the removal of adsorbed particles from, or the deposition of particles on, the surface, is equivalent to the determination of the relation between the amount adsorbed and pressure. In this determination the current density must be so small that the potential of the electrode can be regarded as having its equilibrium value. Such measurements, first made by Shlygin, Ershler, and the author [1-3], led to the unexpected conclusion that the amount of hydrogen absorbed on platinum is, to a first approximation, a linear function of the logarithm of the pressure over a wide range of pressures (e.g., variation in pressure by a factor of about 10^{10}). These results have recently been confirmed by the measurements of Knorr and co-workers [4]. The theory of the logarithmic isotherm has been given by Temkin [5], who showed that the observed relation is to be expected when the adsorption energy falls linearly as the surface becomes covered with adsorbed particles. The cause of this fall could be both the repulsive forces between the adsorbed particles and the heterogeneity of the surface.* Later,

*If we consider the surface to be homogeneous, then the logarithmic isotherm can be explained if we assume that electrons binding adsorbed atoms to the surface are not localized, but are in orbitals that embrace the whole surface. In this case, every extra electron must take up a higher energy level, so that the adsorption energy will fall as the surface coverage increases [6].

by the use of alternating currents of various frequencies, we succeeded in measuring not only the relation of the equilibrium amount of adsorbed hydrogen to the potential, but also the rate at which this equilibrium is disturbed as the potential is displaced owing to the passage of electricity; over a certain range of potentials this rate was found to be approximately independent of potential [7]. In order to explain this it is necessary to assume that, like adsorption energy, the activation energy for the ionization of adsorbed hydrogen at constant potential falls linearly with increase in the coverage of the surface with adsorbed hydrogen and to an extent which is a fractional part of the change in adsorption energy. Electrochemical investigation, therefore, has led to the conclusion that adsorption layers exist in which adsorption energy and activation energy bear a definite relation to surface coverage. This concept was widely applied by Temkin and co-workers in the interpretation of the phenomena of heterogeneous catalysis. On the assumption that the adsorption layers of nitrogen on iron have such properties and that the stage determining the rate of the process as a whole is the stage of chemisorption of N_2 molecules, Temkin [8] succeeded in deriving the following equation for the rate of ammonia synthesis:

$$w = k_1 p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2}\right)^{\alpha} - k_2 \left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{1-\alpha},$$

in which $0 < \alpha < 1$. Of all equations yet proposed, this gives the most satisfactory agreement with the experimental data on this important reaction. The same approach was used by Temkin and co-workers in the determination of the mechanism of transformations of CO and of other heterogeneous processes [9].

Temkin and co-workers later developed a method of studying surface layers which is to a certain extent analogous to the method of charging curves [10]. This method is based on the study of equilibria established as a result of reversible chemical interaction between adsorbed particles and components of the gas phase (for such equilibria the term "adsorptional-chemical equilibrium" has been proposed). Thus, equilibrium between nitrogen adsorbed on an iron catalyst for ammonia synthesis and gaseous hydrogen and ammonia were observed directly:

$$N(ads) + {}^3/_2 H_2(gas) \rightleftharpoons NH_3(gas).$$

As the coverage of the surface with nitrogen increases, the ratio p_{NH_3}/p_{H_2} increases. By combining these results with known values of equilibrium constants for

$$^1/_2 N_2(gas) + {}^3/_2 H_2(gas) \rightleftharpoons NH_3(gas),$$

we obtain the adsorption isotherm for nitrogen. In a similar way, by use of the equilibrium

$$O(ads) + H_2(gas) \rightleftharpoons H_2O(gas)$$

the properties of the surface oxygen of oxides (Fe_3O_4, etc.) were studied.

Like the determination of charging curves, this method can cover a wide range of variation of equilibrium pressures of adsorbed gas, including values inaccessible to direct measurement. The experimental data, both for nitrogen on iron and for surface oxides correspond to the logarithmic adsorption isotherm.

2. Electrocapillary Phenomena and Anomalous Properties of Thin Layers of Liquids

Until recently, two main cases of transition from an adsorbed layer to a new phase were distinguished. In the condensation of vapor on any surface it was assumed that, in the case of complete wetting, as the pressure of the vapor approaches the saturation value, gradual and unlimited increase in the thickness of the adsorbed layer occurs, i.e., the transition from the adsorbed layer to the new phase is continuous. On the other hand, with incomplete wetting the adsorbed layer that is in equilibrium with saturated vapor is substantially different from the bulk phase and is unimolecular or is only a few molecules thick. If a hydrogen or nitrogen bubble is placed at the interface between mercury and electrolyte solution, it has a contact angle which, in the case of an uncharged mercury surface, is about 100° (poor wettability of mercury). From the value of this angle, which depends on the potential of the electrode, we may calculate the interfacial tension at the mercury-bubble interface, on which there is an adsorption layer that is in equilibrium with saturated water vapor [11]. It was found that this inter-

facial tension is also dependent on the potential and follows a certain electrocapillary curve. It follows that this layer contains not only solvent molecules, but also electrolyte ions; it must therefore have a considerable thickness: in a layer that is only 1-2 molecules thick the solvation energy of the ions would be so much reduced that their concentration in equilibrium with the solution would become infinitesimally low. In equilibrium with saturated vapor, therefore, relatively thick layers will be found: they may be dozens of molecules in thickness and yet cannot show a continuous transition into the bulk phase.

These measurements were later repeated with water-alcohol mixtures [12]. Addition of alcohol, which wets the mercury better than water does, results in a further increase in the thickness of the equilibrium layer. In 90% alcohol, the layers obtained give electrocapillary curves that scarcely differ from the usual electrocapillary curve, although the surface tension of mercury in presence of these layers differs by quite an appreciable amount (of the order of one-tenth of an absolute unit) from the tension in presence of liquid in the form of a bulk phase.* I refer to these results because Deryagin and co-workers recently succeeded in showing by optical measurements that as we approach the saturation point the thickness of the adsorbed layer of a polar liquid, e.g., water or an alcohol, on a smooth glass surface does in fact attain a value equivalent to dozens of molecules (up to 100 A), and there is nevertheless a tendency to move to a final limit, i.e., not to grow continuously with transition into the bulk phase; the appearance of the bulk phase is a sudden one [13]. Such anomalies of thin, but not molecularly thin, layers, which were discovered and investigated by Deryagin and co-workers by various other and independent original methods, undoubtedly form a remarkable peculiarity of the liquid state, and we cannot yet give a complete explanation for it.

These examples can be greatly multiplied. Here I will mention only Rebinder's discovery of the electrocapillary effect of change of hardness with polarization and the preparation by Balashova and Bakh of positively charged platinum sols, which became possible when the relation of the sign of the surface charge of platinum to potential was determined by adsorptional-electrochemical methods.

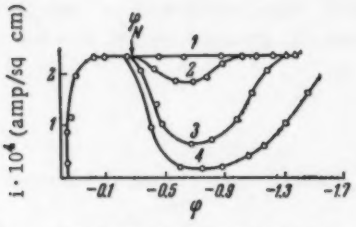


Fig. 1. Relation of current density to potential in 10^{-3} $K_2S_2O_8$ in presence of Na_2SO_4 determined with the aid of rotating amalgamated disc electrode. Potentials referred to the normal hydrogen electrode. φ_N is zero-charge potential. Na_2SO_4 concentration: 1) 1 N; 2) 0.1 N; 3) 0.008 N; 4) 0.

I wish to discuss in greater detail the relationships that I regard as particularly important and the most promising for study at the present time, namely the relationships between electrode processes and ionic reactions in solutions. I shall try to show that comparison of electrochemical data with the results of the investigation of ionic reactions can greatly help in the analysis of reaction mechanisms. In this comparison, however, it must be remembered that the rate of an electrode process is determined by the concentration of particles near the electrode surface, and this may be substantially different from the bulk concentration. This fact can be best illustrated by the behavior of various anions, e.g., persulfate $S_2O_8^{2-}$, in electroreduction at the surface of a mercury or other electrode [14]. The persulfate anion is readily reduced at mercury even with weak cathodic polarization (Figure 1). However, if we pass to more negative potentials at which the mercury surface acquires a negative charge, the rate of reduction falls off sharply and may approach zero at a sufficiently low concentration of supporting electrolyte. This fall in reaction rate is due to lowering of the concentration of the anion in the surface layer resulting from its electrostatic repulsion by the negatively charged surface. The repulsion is eliminated, or at least reduced, by raising the concentration of supporting electrolyte and so screening the electric field of the surface charges and reducing the range of the Coulomb forces. The difference in concentration between the surface layer and the bulk of the solution can be allowed for quantitatively in the case of small ions by introducing the concept of a localized potential (ψ_1-potential) at the center of charge of the reacting particle [15]. In the case of large organic ions and, particularly, neutral molecules, great importance is acquired by effects that depend on the square of the field and are well known from the theory of salting-out of solutes by strong electrolytes [16].

While keeping these differences between bulk and effective concentrations of particles in electrode process

*More accurately, comparison is between the sums of tensions at the mercury-solution and solution-gas boundaries for the cases in which the solution is in the form of a polymolecular layer and in the form of the bulk phase.

in mind, we will examine the catalytic effect of ions on electrode processes. As Iofa, Kabanov, and co-workers have shown [17], hydrogen overvoltage at a mercury cathode falls sharply in presence of adsorbed anions such as bromide and iodide; that is to say, these anions accelerate the electroreduction of a hydrogen ion. This phenomenon, which is the main cause of the relatively low overvoltage in concentrated hydrohalic acids and therefore of their enhanced corrosive action on metals (as shown by, e.g., Heyrovsky [18], Randles [19], and Piontelli [20]), is not confined to the case of the hydrogen ion, but is characteristic for many cases of the electroreduction of cations. Thus, the presence of an adsorbed layer of pentyl alcohol greatly retards the electroreduction of Cd^{2+} and Cu^{2+} ions. However, according to Martirosyan and Kryukova, chloride and bromide ions accelerate this process to such an extent that the inhibiting effect of pentyl alcohol ceases to be noticeable [21].

Antropov [22] made the suggestion, which probably goes too far, that the main cause of the high values of exchange currents for certain metals is their ability to adsorb anions. The catalytic effect of anions disappears or becomes weaker at highly negative potentials, at which the anions cease to be adsorbed. The most elementary explanation of the action of anions that is referred to in Iofa and Kabanov's paper is that the adsorption of an anion causes displacement of the potential in the double layer (ψ-potential) in the negative direction, so that the surface concentration of reacting cations and the rate of reduction are increased. It is possible, however, that anions can participate directly in the electrode process, acting as a carrier of an electron from the electrode to the cation being reduced, a suggestion first made by Heyrovsky.

However we may represent the participation of adsorbed anions in the elementary act, there can be no doubt that they form bridges between the electrode surface and the cation being reduced. Later, the concept of the formation of anion bridges was arrived at by foreign investigators who studied the mechanism of oxidation-reduction processes and isotope exchange in the bulk of a solution with the aid of labeled atoms [23]. Anions, e.g., F^-, Cl^- and OH^-, greatly accelerate processes occurring between cations in solution. The actual mechanism of the action of anions can be represented in various ways. In the case of the oxidation of Cr^{2+} ions with $Co(NH_3)_5Cl^{2+}$, it was shown by the use of labeled chlorine that reaction proceeds with intermediate formation of the activated complex $[Cr-Cl-Co(NH_3)_5]^{2+}$ with transfer of a chlorine atom from cobalt to chromium. It may be supposed that in other cases the role of the anion is to facilitate mutual approach of cations and reaction proceeds by a direct electron transition.

The significance of the formation of anion bridges in reactions with participation of cations is beyond doubt. The question arises of the possibility of the formation of analogous cation bridges in reactions in which anions take part. By the use of labeled atoms it may be shown that a rapid exchange of charges occurs between highly charged anions such as $FeCy_6^{4-}$ and $FeCy_6^{3-}$ or $MoCy_8^{4-}$ and $MoCy_8^{3-}$ [24]. This occurs in spite of the high charges of these anions which, being of the same sign, must create a considerable resistance to the mutual approach of the ions. In explanation of the mechanism of this reaction it was suggested that it proceeds by a tunnel transition of electrons from one reacting particle to another without any direct mutual approach [25]. Some sort of answer to our question may be given by an investigation of the mechanism of the electroreduction of anions at the surface of a negatively charged electrode, which is in many ways analogous to the reaction just mentioned. The more gradual fading off of the electric field at the flat surface of an electrode, as compared with the field around an ion, has the result that the electrostatic repulsive effects must be much more strongly marked in the case of electrode processes. Correspondingly, as I have already mentioned, in the investigation of the electroreduction of anions, considerable retardation of the process is observed when we pass to potentials corresponding to a negatively charged surface. However, at still more negative potentials, in spite of further increase in the negative charge of the surface and therefore in the repulsion of anions, the reaction again acquires a considerable speed (Figure 1). Several arguments can be advanced in support of the view that under these conditions reaction proceeds by tunnel transitions of electrons over distances comparable to the thickness of the double electrical layer. At one time we regarded this suggestion as sound [26], and it is possible that there is some truth in the view. As we shall see below, however, there can be no doubt that the formation of cation bridges plays an important part in the electroreduction of anions. It has already been stated above that the rate of reduction of the persulfate anion increases with increase in the concentration of the supporting electrolyte, i.e., with increase in the concentration of cations in the solution. This effect is all the more notable, the higher the charge of the cation, but I do not wish to discuss this further here because the conclusions that I wish to examine are based on a study of the effect of other factors, namely adsorbability and cation radii.

The data given below are borrowed from the results of Nikolaeva-Fedorovich and co-workers obtained in the Electrochemistry Department of Moscow University. The reduction of persulfate is greatly accelerated if a

surface-active cation, such as the tetrabutylammonium ion, is introduced into the solution [27]. As will be seen from Figure 2, at a concentration of only 10^{-5} N, tetrabutylammonium completely eliminates the anomaly from the polarization curve. Other adsorbable cations behave similarly. However, at sufficiently high negative potentials the effect of tetrabutylammonium disappears and the repulsive effect of the surface on the anion operates in the same way as in the absence of this cation. The key to the understanding of this effect is given by measurements of the capacity of the electrode made with alternating current (lower curve on Figure 2). At the potential at which the action of the organic cation ceases there is a sharp maximum on the capacity curve; this is a desorption peak, indicating that this is the potential marking the limit of the range in which adsorption of the tetrabutylammonium ion occurs. Hence, the tetrabutylammonium ion acts only when it is adsorbed on the electrode surface. The view that the effect of any component of a system on a heterogeneous process e.g., heterogeneous catalysis, can appear only when it is adsorbed at a suitable interface lies at the basis of all the theory of these phenomena, but it is doubtful whether any other methods could give such an unequivocal proof of its correctness. Similar results were obtained for the reduction of the ferricyanide [28] and $HgCy_4^{2-}$ [29] ions.

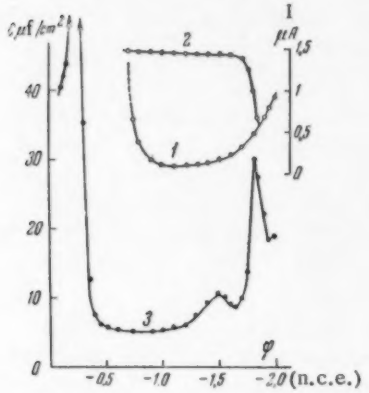


Fig. 2. Relation of current to potential in the electroreduction of the $S_2O_8^{2-}$ anion at a dropping mercury electrode: 1) 10^{-3} N $K_2S_2O_8$; 2) 10^{-3} N $K_2S_2O_8$ + 10^{-5} N $[N(C_4H_9)_4]SO_4$; 3) differential capacity of mercury in 10^{-2} N Na_2SO_4 + 10^{-5} N $[N(C_4H_9)_4]SO_4$.

In the solution of the question raised in this paper, namely the part played by the formation of cation bridges, data on the relation of the effectiveness of cations to their radii are of the greatest importance. Figure 3 shows polarization curves for the electroreduction of 10^{-3} N $K_2S_2O_8$ in presence of 10^{-2} N alkali-metal chlorides (Li^+, Na^+, K^+, Rb^+, and Cs^+ from bottom to top) according to Nikolaeva and Damaskin [27, 30]. These curves were obtained with the aid of a dropping electrode; only parts of the curves corresponding to a negatively charged surface are given in Figure 3, since at positive charges the curve is distorted by a polarographic maximum of the first kind. As will be seen, reaction rate varies greatly with change in the radius of the cation. When a correction is applied to the observed values of the current to take account of changes in concentration due to passage of current, it is found that the rate in presence of 10^{-2} N Cs^+ is about 40 times as great as in presence of Li^+ at the same concentration. A similar relation between the rate of the process and the radius of the cation was found by Zezula for the reduction of the $S_4O_6^{2-}$ anion [31]. As Nikolaeva-Fedorovich showed, a similar relation is observed also in the reduction of the $PtCl_4^{2-}$ anion, which probably proceeds by a somewhat different mechanism.

The dependence of the rate of electrode processes in presence of alkali-metal cations on the radius of the cation was observed earlier (Herasymenko and Slendyk [32] for the electroreduction of hydrogen ions, Izgaryshev and Ravikovich [33], and Vasenin and Gorbachev [34] for the electroreduction of some metal cations). The sign of these effects is opposite to that for the discharge of anions, i.e., the rate of discharge of H^+ ions diminishes as the cation radius increases. In absolute value these effects are relatively small: they are much smaller than the effects observed in the electroreduction of anions. Measurements of electrocapillary curves [35] and particularly the precise measurements of capacity carried out by Grahame [36] have shown that the charge of a negatively charged mercury surface is somewhat dependent on the radius of the cation, and this must lead to differences in the value of the ψ_1-potential and therefore in the kinetics of the processes occurring at the surface. These differences in the rates of reactions in which cations take part may explain the variations in the mean values of the ψ_1-potential, but in the case of the electroreduction of anions the differences in rate are too high to be explained completely without recourse to the concept of a closer interaction between the reacting anion and the cation of the supporting electrolyte, i.e., to the idea of cation bridges. The more readily adsorbed and less highly hydrated Cs^+ ions are found to be more effective than Li^+ ions.

This conclusion is confirmed by measurements of the temperature coefficient of the electroreduction of persulfate [30, 37]. It was found that the temperature coefficient of the rate of this reaction, referred to constant concentration of reactant, falls as we replace the cation of the supporting electrolyte Na^+ by K^+ and particularly

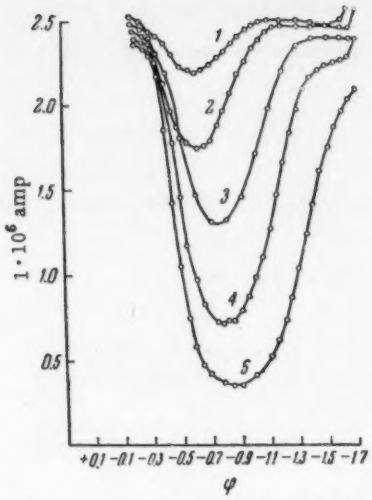


Fig. 3. Relation of current at dropping electrode to potential in 10^{-3} N $K_2S_2O_8$ in presence of 10^{-2} alkali-metal chloride: 1) CsCl; 2) RbCl; 3) KCl; 4) NaCl; 5) LiCl.

by Cs^+, which indicates increase in the strength of the bond formed with the anion in this order. In the case of a Cs^+ supporting electrolyte, the temperature coefficient of the reaction becomes negative. Analogous conclusions are reached by a comparison of the rates of electroreduction of the BrO_3^- anion in supporting electrolytes containing various cations [38]. The formation of cation bridges has been recently confirmed by a comparison of differential capacities of the electrode in presence of the chlorides and iodides of sodium and cesium [39].

In a paper read in 1955 at a conference on chemical kinetics, I expressed regret at the absence of data on salt effects in bulk reactions between anions which could throw light on why electrostatic repulsion does not prevent rapid reaction in these cases [40]. In 1957 there appeared a paper by the American authors Sheppard and Wahl [41], who investigated the kinetics of exchange between MnO_4^{2-} and MnO_4^- and showed that the rate of this process is greatly dependent on the nature of the cation, which led them to suggest that a cation bridge of the type $[MnO_4-K-MnO_4]^{2-}$ plays a part in the reaction, a suggestion analogous to that made by us on the basis of electrochemical data.*

The effectiveness of cations in the formation of cation bridges is not determined entirely by their adsorbability and hydration energy, but probably depends also on relations between the dimensions of the cation and the distance at which the center of the activated complex will be found in the transition of an electron from the electrode surface to the anion being reduced. Large organic cations such as $N(C_4H_9)_4^+$, which accelerate the reduction of the anions $S_2O_8^{2-}$, $FeCy_6^{3-}$, and $HgCy_4^{2-}$ to an extremely high degree at potentials corresponding to the minimum of the polarization curve, do not accelerate, but even retard, the reduction of $PtCl_4^{2-}$ [28]. It is possible that, owing to the planar configuration and, probably, high adsorbability of this anion, the transition of an electron in the reduction proceeds at a much shorter distance from the electrode surface than in the reduction of the anions already discussed, and the positive charge of the cation, which is at a relatively great distance from the electrode surface, is ineffective. Only at higher negative potentials, at which, judging from measurements of differential capacity, there appears to occur some flattening of the tetrabutylammonium cation at the electrode surface, is some acceleration of the process observed, and this disappears at still more highly negative potentials owing to the desorption of the cation from the surface.

I have tried to illustrate the relation between electrochemical kinetics and the kinetics of ionic reactions in the bulk of a solution with the aid of examples of processes proceeding with the participation of anions. Of no less interest would be a comparison of phenomena of acid-base catalysis with discharge of hydroxonium ions and other proton donors at electrode surfaces, but this is outside the scope of the present paper.

LITERATURE CITED

[1] A.I. Shlygin and A.N. Frumkin, Acta Phys. Chim. URSS 3, 791 (1935); A.I. Shlygin, A.N. Frumkin and V.I. Medvedovsky, Acta Phys. Chim. URSS 4, 911 (1936); A.N. Frumkin and A.I. Shlygin, Bull. Acad. Sci. USSR, chem. ser. 773 (1936).

*The authors mention also the possibility that the action of cations is determined by changes in the activities of the reactants and the transition complex (analogous to the assumption that the effects observed by Nikolaeva-Fedorovich and Damaskin depend on change in the mean value of the ψ_1-potential). In any case, the role of the cation must consist essentially in the facilitation of the mutual approach of anions, since the transition of an electron from an MnO_4^{2-} ion to, e.g., a K^+ ion is not very probable. This applies also to the effect of cations on electroreduction, at least in those reactions in which, like the electroreduction of $PtCl_4^{2-}$, they occur at not very negative potentials, at which the conversion of an adsorbed cation into an atom is energetically unfavorable. It may be noted that at a much earlier date it was shown that the reaction between $S_2O_3^{2-}$ and $C_2H_2BrO_2^-$ is accelerated in presence of La^{3+} cations [42].

[2] B.V. Ershler, Acta Phys. Chim. URSS 7, 327 (1937); B.V. Ershler, G.A. Deborin and A.N. Frumkin, Bull. Acad. Sci. USSR, chem. ser. 1065 (1937); B. Ershler and A. Frumkin, Trans. Faraday Soc. 35, 1 (1939).

[3] A.N. Frumkin, J. Phys. Chem. 14, 1200 (1940); Problems of Kinetics and Catalysis 6, 85 (1949).

[4] M. Breiter, C.A. Knorr and W. Völkl, Z. Elektrochem. 59, 681 (1955).

[5] M.I. Temkin, J. Phys. Chem. 15, 296 (1941); M.I. Temkin and V.G. Levich, J. Phys. Chem. 20, 1441 (1946).

[6] M.I. Temkin, Questions of Chemical Kinetics, Catalysis and Reactivity (Izd. AN SSSR, Moscow, 1955), p. 484.*

[7] P.I. Dolin and B.V. Ershler, J. Phys. Chem. 14, 886 (1940); P.I. Dolin, B.V. Ershler and A.N. Frumkin, J. Phys. Chem. 14, 907 (1940).

[8] M.I. Temkin and V.M. Pyzhev, J. Phys. Chem. 13, 851 (1939); M.I. Temkin and S.L. Kiperman, J. Phys. Chem. 21, 927 (1947); M.I. Temkin, J. Phys. Chem. 24, 1312 (1950); V.D. Livshits and I.P. Sidorov, J. Phys. Chem. 26, 538 (1952).

[9] N.V. Kulkova and M.I. Temkin, J. Phys. Chem. 23, 695 (1949); M.I. Temkin, J. Phys. Chem. 31, 3 (1957).

[10] A.E. Romanushkina, S.L. Kiperman and M.I. Temkin, J. Phys. Chem. 27, 1181 (1953); N.V. Kulkovai and M.I. Temkin, J. Phys. Chem. (in the press).

[11] A.N. Frumkin, A.V. Gorodetskaya, B.N. Kabanov and N.I. Nekrasov, J. Phys. Chem. 3, 351 (1932); A.N. Frumkin, J. Phys. Chem. 12, 337 (1938); A.N. Frumkin and A.V. Gorodetskaya, J. Phys. Chem. 12, 511 (1938); B.N. Kabanov and N. Ivanishchenko, Bull. Acad. Sci. USSR, div. math. nat. sci. 756 (1936).

[12] I.P. Tverdovsky and A.N. Frumkin, J. Phys. Chem. 21, 819 (1947).

[13] B.V. Deryagin and Z.M. Zorin, J. Phys. Chem. 29, 1010, 1755 (1955).

[14] T.A. Kryukova, Proc. Acad. Sci. USSR 65, 517 (1949); A.N. Frumkin and G.M. Florianovich, Proc. Acad. Sci. USSR 80, 907 (1951); T.V. Kalish and A.N. Frumkin, J. Phys. Chem. 28, 473 (1954); N.V. Nikolaeva, N.S. Shapiro and A.N. Frumkin, Proc. Acad. Sci. USSR 86, 581 (1952); N.V. Nikolaeva and A.A. Grossman, Proc. Acad. Sci. USSR 95, 1013 (1954); G.M. Florianovich and A.N. Frumkin, J. Phys. Chem. 29, 1827 (1955); A.N. Frumkin and N.V. Nikolaeva, J. Chem. Phys. 26, 1552 (1957).

[15] A. Frumkin, Z. Phys. Chem. (A) 164, 121 (1933).

[16] A. Frumkin, Z. Phys. 35, 792 (1926); E.P. Andreeva, J. Phys. Chem. 29, 699 (1955).

[17] Z.A. Iofa, B.N. Kabanov, E.M. Kuchinsky and F. Chistyakov, J. Phys. Chem. 13, 1105 (1939).

[18] J. Heyrovsky, Disc. Faraday Soc. 1, 212 (1947).

[19] J. Randles and K. Somerton, Trans. Faraday Soc. 48, 937, 951 (1952).

[20] R. Piontelli, Comptes. rend. 2-me Reunion CITCE, 1951).

[21] A.P. Martirosyan and T.A. Kryukova, J. Phys. Chem. 27, 851 (1953).

[22] L.I. Antropov, Progr. Chem. 25, 1043 (1956).

[23] W. Libby, J. Phys. Chem. 56, 863 (1952); H. Taube, H. Meyers and R. Rich, J. Am. Chem. Soc. 75, 4118 (1953); H. Taube and H. Meyers, J. Am. Chem. Soc. 76, 2103 (1954); H. Taube and E.L. King, J. Am. Chem. Soc. 76, 4053 (1954); R. Murman, H. Taube and F. Posey, J. Am. Chem. Soc. 79, 262 (1957); B. Zwolinski, R. Marcus and H. Eyring, Chem. Rev. 55, 157 (1955); M. Haissinsky, J. Chim. Phys. 48, 1 (1951).

[24] J. Cobble and A. Adamson, J. Am. Chem. Soc. 72, 2276 (1950); R. Wolfgang, J. Am. Chem. Soc. 74, 6144 (1952).

[25] H. Taube, Ann. Rev. Phys. Chem. 4, 290 (1953); R. Marcus, B. Zwolinski and H. Eyring, J. Phys. Chem. 58, 432 (1954).

*In Russian.

[26] A.N. Frumkin, Progr. Chem. 24, 933 (1955).

[27] N.V. Nikolaeva-Fedorovich and B.B. Damaskin, Trans. Conference on the Effect of Surface-Active Agents on the Electrodeposition of Metals (Vilna, 1957), p. 33*; A.N. Frumkin, Trans. Fourth Conference on Electrochemistry (in the press).

[28] L.A. Fokina, Diploma thesis, Chem. Dept. Moscow State Univ. 1957.*

[29] J. Siekierski, Roczniki Chemii 30, 1083 (1956).

[30] N.V. Nikolaeva-Fedorovich and B.B. Damaskin, Trans. Fourth Conference on Electrochemistry (in the press).*

[31] J. Zezula, Chem. Listy 47, 492, 1303 (1953).

[32] P. Herasymenko and I. Slendyk, Z. Phys. Chem. (A) 149, 123 (1930).

[33] N.A. Izgaryshev and Kh.N. Ravikovich, J. Russ. Phys. Chem. Soc., chem. sect. 62, 255 (1930).

[34] R.M. Vasenin and S.V. Gorbachev, J. Phys. Chem. 28, 2156 (1954).

[35] M. Gouy, Ann. Chim. et Phys. 29, 145 (1903).

[36] D.C. Grahame, J. Electrochem. Soc. 98, 343 (1951); D.C. Grahame, E.M. Coffin, J.L. Gummings and M.A. Poth, J. Am. Chem. Soc. 74, 1207 (1951); D.C. Grahame, Compt. rend. 3-me Reunion (CITCE, Milano), p. 336.

[37] A.N. Frumkin and N.V. Nikolaeva-Fedorovich, Buil. Moscow State Univ., phys. math. chem. ser. (in the press).

[38] V.I. Zykov and S.I. Zhdanov, J. Phys. Chem. (in the press).

[39] A.N. Frumkin, B.B. Damaskin and N. V. Nikolaeva-Fedorovich, Proc. Acad. Sci. USSR 115, 751 (1957).**

[40] A.N. Frumkin, Questions of Chemical Kinetics, Catalysis and Reactivity (Izd. AN SSSR, Moscow, 1955), p. 402.*

[41] J. Sheppard and A. Wahl, J. Am. Chem. Soc. 79, 1020 (1957).

[42] V. La Mer and M. Kamner, J. Am. Chem. Soc. 57, 2662 (1935).

Received October 1, 1957

Institute of Physical Chemistry
Academy of Sciences, USSR

*In Russian.

**Original Russian pagination. See C.B. translation.

NITRATION OF FLUOROOLEFINS WITH NITROGEN DIOXIDE

I.L. Knunyants and A.V. Fokin

(Paper read at a session of the Division of Chemical Sciences of the Academy of Sciences of the USSR, October 30, 1957)

The nitration of aromatic and of saturated and unsaturated aliphatic hydrocarbons has been extensively studied and developed, but the nitration of fluoro compounds has scarcely been investigated at all. The study that we have undertaken of the nitration of fluoroolefins with oxides of nitrogen has established the existence of differences in the reactivities of various fluoroolefins and has led to the synthesis of several previously unknown fluoro compounds, including fully fluorinated 2-nitroalkyl nitrites, the chemistry of which is unusual and interesting.

It is known that fluoroolefins, like other olefins carrying electronegative substituents such as acrylic acid, acrolein, and nitroethylene, readily combine with nucleophilic reagents, such as ammonia, thiols, and sodium bisulfite, which, under the same conditions, do not add to an isolated ethylenic bond.

Most of the reactions of fluoroolefins with nucleophilic reagents are ionic in character, and their first stage must be regarded as an attack by an anion. Such a view is supported by the necessity for alkaline catalysis in almost every case of the addition of a substance having only weakly nucleophilic properties to fluoroolefins [1-4].

In contrast to the smooth reaction of perfluoroolefins with nucleophilic reagents, the addition of which proceeds more readily as the polarity of the double bond is increased, reaction with electrophilic reagents can be effected only under very much more severe conditions. Many reactions of fluoroolefins proceed with great difficulty and only with free-radical initiation.

The reactions of fluoroolefins with halogen compounds, hydrohalic acids, and especially fully fluorinated iodoalkanes, and also their polymerization, proceed by free-radical mechanisms and demand the supply of energy (for the homolytic breakdown of reactants and the crossing of the energy barrier) in the form of heat, light, or catalytically acting additions, e.g., peroxy compounds and other initiators for free-radical processes. These peculiarities of fluoroolefins are probably associated with electronic exhaustion of the π-bond as a result of the specific electronegativity of fluorine. With agents that readily form free radicals and with radical-like molecules perfluoroolefins should therefore react smoothly. In view of these considerations, the behavior of perfluoroolefins toward nitrogen dioxide is of special interest.

Coffman in 1949 and Haszeldine in 1953 [5-7] stated that in the reactions of tetrafluoroethylene and of chlorotrifluoroethylene with nitrogen dioxide only dinitroalkanes are formed; they did not investigate reaction with other fluoroolefins. In our investigation of the nitration of perfluoroolefins with nitrogen dioxide we showed that the course of this reaction depends to a considerable extent on the structure and peculiarities of the fluoroolefin and can give not only dinitro compounds, but also some new interesting substances.

In the gas phase and in nonpolar and only slightly polar solvents, nitrogen dioxide dissociates with formation of radical-like NO_2 molecules. The radical character of the NO_2 molecule is confirmed by its paramagnetism, its line absorption spectrum, its color, and the readiness with which it reacts with species carrying an unpaired electron. Nitrogen dioxide monomer has seventeen valence electrons. The unpaired electron may be found either on the nitrogen atom or on one of the oxygen atoms, so that it is logical to expect not only NO_2

particles will add at the double bond, but also ONO particles with formation of fully fluorinated nitroalkyl nitrites. It is formally possible that addition of two nitrite groups may occur with formation of fully fluorinated alkylene dinitrites.

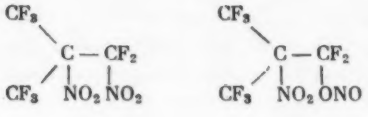
We showed that reaction between tetrafluoroethylene and nitrogen dioxide in a confined space is explosive [8-9]. A controllable reaction can be brought about in inert solvents of low polarity, such as carbon tetrachloride, dichlorotetrafluoroethane, etc. The main reaction products, formed in 80% yield, then consist in a mixture of tetrafluoro-1,2-dinitroethane and tetrafluoro-2-nitroethyl nitrite. In addition, a small amount of a mixture of high-boiling telomerization products of tetrafluoroethylene is formed under the initiating action of nitrogen dioxide:

$$CF_2=CF_2 + N_2O_4 \rightarrow \begin{matrix} O_2NCF_2-CF_2-ONO \\ O_2NCF_2-CF_2-NO_2 \\ O_2N(CF_2)_nNO_2 \\ NO_2CF_2-CF_2-N=O. \end{matrix}$$

The dinitro compound and the nitro nitrite were obtained in almost equal amounts. In the reaction of tetrafluoroethylene with nitrogen dioxide in the gas phase at about 100° at ordinary pressure, in addition to tetrafluoro-1,2-dinitroethane and tetrafluoro-2-nitroethyl nitrite, tetrafluoro-1-nitro-2-nitrosoethane was obtained.

We succeeded in extending nitration with nitrogen dioxide to other perfluoroolefins [8]. It was found that in the nitration of perfluoropropene and perfluoroisobutene more severe conditions were required (absence of solvent and elevated temperature). Perfluoropropene is nitrated in good yield at 90-100° and perfluoroisobutene at 160-180°. In the first case almost the only product formed is hexafluoro-2-nitropropyl nitrite (yield more than 90%), with only a small amount of hexafluoro-1,2-dinitropropane, but when the temperature is raised to 150° the yield of hexafluoro-1,2-dinitropropane is increased from 5% to 15-20%.

In the case of perfluoroisobutene [pentafluoro-2-(trifluoromethyl)propene] the main reaction products are pentafluoro-1,2-dinitro-2-(trifluoromethyl)propane and pentafluoro-2-nitro-2-(trifluoromethyl)propyl nitrite (in equal amounts):



Nitration of perfluorocyclobutene with nitrogen dioxide can be carried out within a comparatively narrow temperature range. Reaction does not go below 130-140°, and above 170° the mixture explodes. The reaction gave hexafluoro-1,2-dinitrocyclobutane and perfluorosuccinyl fluoride.

TABLE 1

Formula	B.p. °C	d_4^{20}	n_D^{20}	Found %		Calc. %	
				F	N	F	N
$O_2NCF_2-CF_2NO_2$	57–58	1.622	1.3249	39.4	14.2	39.6	14.6
$O_2NCF_2-CF_2-ONO$	17	1.5310	1.3002	39.6	14.9	39.6	14.6
$CF_3-CF(NO_2)-CF_2NO_2$	76	1.6313	1.3141	37.4	10.9	37.1	11.5
$CF_3-CF(NO_2)CF_2-ONO$	57	1.637	1.3276	47.0	11.5	45.9	11.0
$(CF_3)_2C(NO_2)CF_2-NO_2$	92	1.660	1.3212	52.0	—	52.1	—
$(CF_3)_2C(NO_2)CF_2-ONO$	48	1.598	1.2870	52.0	—	52.1	—
$CF_2-CF(NO_2)CF(NO_2)CF_2$	62/100	1.7721	1.3640	44.5	10.2	45.3	11.0

It was thus shown that perfluoroolefins (tetrafluoroethylene, perfluoropropene, perfluorocyclobutene, and perfluoroisobutene) react with nitrogen dioxide with varying ease with formation of fully fluorinated 1,2-dinitroalkanes and fully fluorinated 2-nitroalkyl nitrites.

Comparison of the rates of reaction with nucleophilic compounds (alcohols, thiols, etc.) makes it possible to place fluoroolefins in a series, in which tetrafluoroethylene is the least reactive:

$$CF_2=CF_2<CF_3-CF=CF_2<\begin{matrix}CF_3\\CF_3\end{matrix}\!\!>C=CF_2$$

As is well known, tetrafluoroethylene reacts with alcohols and thiols above 100° and in presence of alkaline catalysts; with perfluoroisobutene the same reactions proceed readily in the cold without catalysts. As would be expected, for the reaction of perfluoroolefins with the electrophilic nitrogen dioxide the relative behaviors are different. The compound most reactive toward N_2O_4 was found to be tetrafluoroethylene, and as we pass from this to perfluoropropene and perfluoroisobutene the difficulty of nitration greatly increases. In reactivity toward nitrogen dioxide the perfluoroolefins can be arranged in the following series:

$$CF_2=CF_2>CF_3-CF=CF_2>\overline{CF_2-CF=CF-CF_2}>\begin{matrix}CF_3\\CF_3\end{matrix}\!\!>C=CF_2$$

Their reactivity toward nitrogen dioxide is therefore in accord with the behavior observed in other known cases of the free-radical addition of electrophilic reagents [10].

The conditions required for nitration and the character of the products indicate that the reaction has a free-radical mechanism. The following facts provide proof of this: the reaction proceeds in nonpolar solvents, i.e., under conditions favoring homolytic processes; reaction is not accelerated by addition of strong acids to the reaction mixture, and in some cases the degree of conversion and the yield of nitration products are lowered; telomerization of fluoroolefins, initiated by radical NO_2 molecules, is observed in the nitration reaction; fluoroolefins can be nitrated in the gas phase at elevated temperatures with formation of nitro nitrites, dinitro compounds, and nitroso compounds; in some cases in absence of solvents chain reactions occur and may result in explosions; and so on.

The use of solvents favoring ionic reactions, e.g., nitrobenzene, did not affect the composition of the reaction products. On addition of strong acids (nitric, sulfuric, and hydrofluoric), in presence of which N_2O_4 dissociates into the nitroso cation NO^+ and the nitrate anion $O-N\begin{matrix}O\\O\end{matrix}$, the products detected were again only those resulting from the addition of products of the homolytic dissociation of N_2O_4: tetrafluorodinitroethane and tetrafluoro-2-nitroethyl nitrite, but not tetrafluoronitrosoethyl nitrate, the formation of which would be evidence of an ionic process.

We proved experimentally that free radicals are formed by the action of nitrogen dioxide on perfluoroolefins. The proof was based on bringing the tetrafluoronitroethyl radical formed in the process into reactions specific for free radicals with a third component, not in itself reactive toward the original olefin. A mixture of equal volumes of tetrafluoroethylene, nitrogen dioxide, and nitric oxide was passed through a glass or nickel tube at 100-130° and, apart from products of the addition of N_2O_4 (tetrafluorodinitroethane and tetrafluoro-2-nitroethyl nitrite), tetrafluoro-1-nitro-2-nitrosoethane ($NO_2-CF_2-CF_2-NO$) was formed.

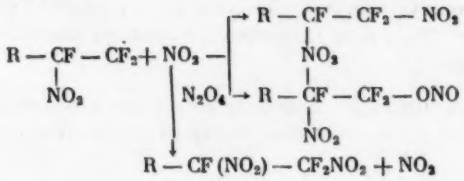
The reaction of tetrafluoroethylene with nitric oxide in presence of NO_2 proceeds by the combination of the intermediate tetrafluoronitroethyl radical and NO molecules, which have a hidden radical function. Moreover, the fact that in this reaction the fully fluorinated nitronitrosoalkane is formed and none of the corresponding nitroso nitrite confirms the view that the primary act in the reaction is attack of the double bond of the fluoroolefin by NO_2 and not by ONO. The formation of nitroso compounds in this reaction shows that the two NO_2

molecules do not add at the same time, as otherwise the formation of mixed nitroso compounds would be impossible.

The reaction of perfluoroolefins with nitrogen dioxide in the gas phase or in a nonpolar solvent results from interaction between electrons of the π-bond and radical-like nitrogen dioxide monomer:

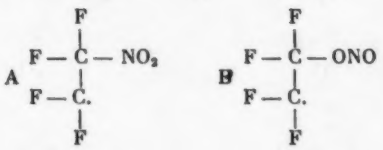
$$CF_2 = CF_2 \xrightarrow{NO_2} O_2NCF_2 - \dot{C}F_2.$$

The resulting fully fluorinated nitroalkyl radical reacts with NO_2 molecules (or N_2O_4 molecules if they can be present under the conditions of reaction):

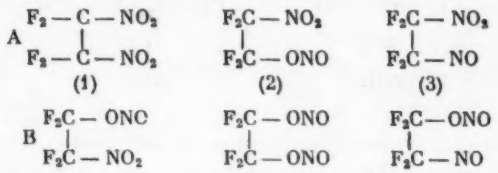


The nitrogen dioxide molecule can add to a carbon atom with formation of C–N or C–O bonds (fully fluorinated 1,2-dinitroalkane or 2-nitroalkyl nitrite). The second stage of reaction, therefore, consists in the combination of the intermediate radical with the radicals NO_2, ONO, and, in some cases, NO. This recombination process is rapid and does not require appreciable activation. The kinetics of the reaction are determined by the rate of the first stage.

Each of the two theoretically possible radicals A and B



which may be formed in the initial stage of the reaction may be stabilized by addition of one of the radicals ONO or NO; this addition may give the following compounds:



Whatever procedure was used in the reaction of tetrafluoroethylene with nitrogen dioxide, the formation of compounds (2) and (3) of series B was never observed, whereas addition of type A gave all the substances (1), (2), and (3) of series A and these we isolated and investigated.

The formation of tetrafluoro-1,2-dinitroethane, tetrafluoro-2-nitroethyl nitrite, and tetrafluoro-1-nitro-2-nitrosoethane in the reaction of tetrafluoroethylene under various conditions indicates that the primary act is attack by NO_2 radicals. The absence of dinitrites in the nitration of various perfluoroolefins is an indication of the analogous character of the primary act in these reactions.

The formation of products of high molecular weight in the nitration of tetrafluoroethylene probably proceeds as an unbranched chain reaction:

$$CF_2 = CF_2 + \cdot NO_2 \rightarrow F_2C(NO_2) - \dot{C}F_2 \xrightarrow{n(CF_2=CF_2)}$$

$$\rightarrow F_2C(NO_2)-CF(CF_2-CF_2)\dot{n} \xrightarrow[ONO]{NO_2} CF_2(NO_2)-CF_2(CF_2CF_2)_nNO_2$$

or

$$CF_2(NO_2)-CF_2(CF_2-CF_2)_nONO$$

Owing to the high stability of the fluorine-carbon bond and of compounds containing several fluorine atoms on a carbon atom, the nitration products of fluoroolefins undergo no changes in the reaction zone and can be readily isolated in absence of moisture. Thus, fully fluorinated 2-nitroalkyl nitrites, unlike the unfluorinated compounds, were found to be quite stable.

Fully fluorinated 2-nitroalkyl nitrites are formed not only in the liquid phase, but also in the gas phase. Thus, tetrafluoro-2-nitroethyl nitrite is formed at 100-140° by gas-phase nitration, and hexafluoro-2-nitropropyl nitrite is formed at about 200°.

We showed that the degradation of tetrafluoro-2-nitroethyl and hexafluoro-2-nitropropyl nitrites occurs only above 250°. The stability of these compounds can be explained by the impossibility of the intramolecular oxidation that is peculiar to unsubstituted nitrites.

In the case of unsymmetrical perfluoroolefins, e.g., perfluoropropene, there are two possible ways for nitrogen dioxide to add and these would give the hexafluoronitropropyl nitrites (I) and (II):

$$CF_3-CF(NO_2)-CF_2-ONO \quad (I) \qquad CF_3-CF(ONO)-CF_2NO_2 \quad (II)$$

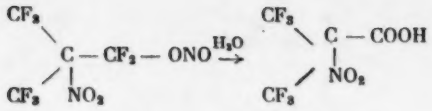
By reaction with water (I) could give tetrafluoro-2-nitropropionic acid (III), whereas (II) would be expected to give pentafluoronitroacetone (IV):

$$CF_3-CF(NO_2)-COOH \quad (III) \qquad CF_3-C(=O)-CF_2-NO_2 \quad (IV)$$

The formation of tetrafluoro-2-nitropropionic acid as the only product of the hydrolysis of hexafluoronitropropyl nitrite confirmed the direction of the addition of the nitro and nitrite groups to perfluoropropene: the nitro group adds to the central carbon atom, which carries the lowest number of fluorine atoms. As would be expected, addition to perfluoropropene is in the direction opposite to that for addition to unsubstituted propene. Perfluoroisobutene appears to be a more polar fluoroolefin and reacts in the cold with alcohols, amines, and other nucleophilic reagents. The chemical peculiarities of perfluoroisobutene are reflected also in its reactions with electrophilic reagents; the difficulty with which these occur has been shown in the case of bromine and iodine. The free-radical reaction of addition of nitrogen dioxide to this olefin is also very sluggish.

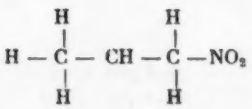
The nitration of perfluoroisobutene was carried out in absence of solvents, and good yields could be obtained only at 170-180°. There were two main products: pentafluoro-1,2-dinitro-2-(trifluoromethyl)propane and pentafluoro-2-nitro-2-(trifluoromethyl)propyl nitrite, formed in approximately equal amounts in an overall yield of about 90%.

In this case the direction of addition of nitro and nitrite groups was again established by conversion of the pentafluoro-2-nitro-2-(trifluoromethyl)propyl nitrite into trifluoro-2-nitro-2-(trifluoromethyl)propionic acid and its derivatives:

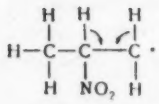


As in the case of perfluoropropene, in the reaction with perfluoroisobutene the nitro group added at the least fluorinated carbon atom.

It is known that reaction of nitrogen dioxide with the usual olefins at 0° in presence of oxygen and solvents results in the formation of vicinal dinitroalkanes and nitroalkyl nitrites, which are readily oxidized to nitrates [11-13]. In these reactions with unsymmetrical olefins, specific orientation of the attack of nitrogen dioxide monomer particles is observed and it results in the formation of nitro nitrites in which the nitro group is always attached to the carbon atom having the highest electron density. In the investigation of the nitration products from unsymmetrical fluoroolefins we showed that in the fully fluorinated 2-nitroalkyl nitrites the nitro group adds at the least fluorinated carbon atom in the position of highest electron density. In the addition of NO_2 and ONO to unsubstituted propene or isobutene, the primary act is the addition of NO_2 at the position of highest electron density. The radical formed (1), owing to the conjugation of the unpaired electron with the electrons of five C–H bonds is more stable than the radical (2), in which the unpaired electron is conjugated only with one C–H bond:



(1)



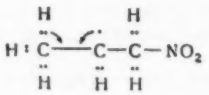
(2)

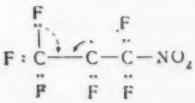
In this case, of course, radical (1) is formed, and as a result of recombination with other particles it gives addition products of the type:

$H_3C - CH(X) - CH_2 - NO_2$,
where $X = NO_2$, ONO, NO.

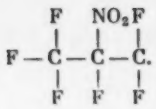
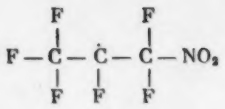
The extension of concepts of bond conjugation in ordinary olefins to perfluoroolefins requires some discussion.

It is probable that, in the case of perfluoropropene and perfluoroisobutene, owing to the displacement of the electron pairs forming C–F bonds in the direction of the fluorine atoms, the conjugation of the free electron with the electrons of these σ-bonds in the β-position is less readily realized:

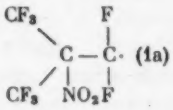
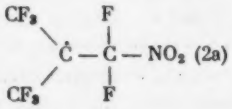




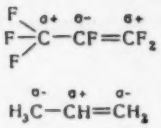
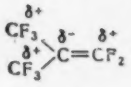
Owing to the closeness of the values of the covalent radii of fluorine and carbon, the maximum coordination of the unpaired electron in the intermediately formed radical occurs in the difluoromethylene group CF_2, which, in this case, can probably be regarded as a five-electron system. As a result of this peculiar conjugation of the two radicals that are probably formed during the attack of an unsymmetrical perfluoroolefin by nitrogen dioxide, (1) will be the more stable, not (2), in which the probability of such conjugation is lower:

Conjugation of the free electron in the intermediate radical (II), which arises by the action of NO_2 on perfluoroisobutene, is very difficult, whereas it is readily realized in the radical (I):


(1a)

(2a)

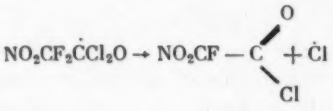
Also, in perfluoropropene and perfluoroisobutene, as a result of the conjugation of the fluorine atoms of the trifluoromethyl groups, polarization is in a direction opposite to that in the corresponding unsubstituted olefins:

Nitrogen dioxide is an electrophilic agent, and its dipole moment varies with the temperature from 0.3 to 0.58 D [14]; it therefore tends to add to the double bond at the carbon having the highest electron density. Such addition will give an intermediate radical of type (I). In our case the fact that nitrogen dioxide adds to the fluoromethylidyne of perfluoropropene and to the carbon atom not attached to fluorine in perfluoroisobutene is the result, on the one hand, of the high stability of the radicals formed and, on the other, of the electrophilic character of the nitrogen dioxide molecule and the polarity of the perfluoroolefins.

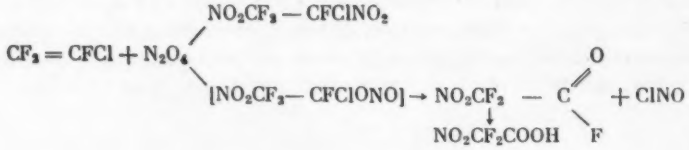
Investigation of the nitration of chlorofluoroolefins, namely chlorotrifluoroethylene, 1,2-dichlorodifluoroethylene, and 1,1-dichlorodifluoroethylene, revealed some peculiar features of this reaction, considered in relation to the corresponding reaction of fully fluorinated olefins.

Nitration of chlorofluoroolefins with nitrogen dioxide gives stable dinitro compounds and the corresponding nitro nitrites, which are much less stable than fully fluorinated 2-nitroalkyl nitrites. The stability of the RO–NO bond in the nitrites formed is found to be too low for them to be isolated in the individual state. Elimination of NO from a nitro nitrite results in the formation of a substituted alkoxy radical, e.g., $NO_2CF_2CCl_2O$, which stabilizes itself by liberation of atomic chlorine:



The NO and atomic chlorine combine to form a molecule of nitrosyl chloride, which then reacts with the original chlorofluoroolefin with formation of chlorination, nitrosation, and nitration products.

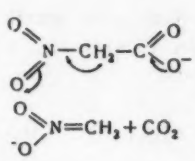
The addition of nitrogen dioxide to chlorotrifluoroethylene proceeds smoothly in tetrachloroethane and other solvents at room temperature (in absence of solvent the reaction is explosive). The following substances were isolated from the reaction mixture: chlorotrifluoro-1,2-dinitroethane, 1,2-dichloro-1,1,2-trifluoro-2-nitrosoethane, 1,2-dichloro-1,1,2-trifluoroethane, difluoronitroacetal fluoride, and high-boiling telomerization products:

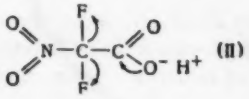


$$ClNO + ClCF = CF_2 \rightarrow CF_2Cl - CFClNO$$
$$CF_2Cl - CFClNO_2$$
$$CF_2Cl - CFCl_2.$$

As already stated, fully fluorinated 2-nitroalkyl nitrites are stable compounds. Whereas ordinary nitroalkyl nitrites react with water and alcohols with formation of nitro alcohols, fully fluorinated nitroalkyl nitrites, treated with the same reagents, undergo more complex changes associated with the presence of fluorine in the molecule. Fully fluorinated 2-nitroalkyl nitrites are hydrolyzed to fully fluorinated α-nitro carboxylic acids, which are more stable than ordinary α-nitro acids and are not decarboxylated even by distillation under ordinary pressure; thus by repeated distillation, it is possible to obtain anhydrous difluoronitroacetic acid, which forms hygroscopic clear colorless crystals, m.p. 37° [9].

The readiness with which nitroacetic acid is decarboxylated is probably due to the fixation of a proton by an oxygen of the nitro group, the electron density of which is considerably increased by conjugation. Such conjugation, of course, is almost absent in difluoronitroacetic acid owing to the electron-attracting effect of fluorine atoms, this being the explanation of the stability of fully fluorinated α-nitro carboxylic acids.


(I)


(II)

Hydrolysis of hexafluoro-2-nitropropyl nitrite and of pentafluoro-2-nitro-2-(trifluoromethyl)propyl nitrite with the calculated amounts of water gives tetrafluoro-2-nitropropionic and trifluoro-2-nitro-2-(trifluoromethyl)-propionic acids, respectively. These acids also are found to be stable compounds (readily distilled at ordinary pressures).

Tetrafluoro-2-nitropropionic acid was converted into several esters by esterification in the usual way; these esters can be hydrolyzed back to the original tetrafluoro-2-nitropropionic acid. Difluoronitroacetic esters are also readily prepared by the action of alcohols on the anhydride or acid chloride, but it was found that the most convenient way of preparing these esters is direct reaction between tetrafluoro-2-nitroethyl nitrite and alcohols. This new method was extended to other fully fluorinated nitroalkyl nitrites.

In unsubstituted alkyl nitrites the most labile link is the RO–NO bond [15]. The energy required for the rupture of this bond is about 20 kcal/mole less than that required for the rupture of the R–ONO or $R-NO_2$ bond [13].

R	D(R–NO_2) (kcal/mole)	D(R–ONO) (kcal/mole)	D(RO–NO) (kcal/mole)
Methyl	53.7	56.2	38.9
Ethyl	56.1	57.8	38.4
n-Propyl	59.7	61.0	39.6
n-Butyl	61.0	–	37

The possibility of preparing fully fluorinated 2-nitroalkyl nitrites in the gas phase at high temperature (which has been shown in the present investigation) indicates that the $O_2NRO-NO$ bond is of comparatively high stability in these compounds. However, as in alkyl nitrites, this bond is weaker than the others (R–ONO or $R-NO_2$) in the nitrous ester molecule. Confirmation of this is found in the fact that the NO ion of mass number 30 gives the greatest intensity in the mass spectrum of tetrafluoro-2-nitroethyl nitrite.

Heterolytic dissociation of tetrafluoro-2-nitroethyl nitrite can occur with formation of a nitrosyl cation. Correspondingly, the hydrolysis of the nitrous ester, which proceeds rapidly with evolution of heat, can be represented as a series of successive reactions that include initial elimination of an NO^+ ion:

$$O_2N-CF_2-CF_2-O-N=O + HOH \rightarrow [O_2N-CF_2-CF_2-OH] + HONO$$

$$O_2NCF_2CF_2OH \rightarrow NO_2CF_2-\overset{\overset{O}{\|}}{C}-F + HF$$

$$O_2NCF_2COF \xrightarrow{HOH} O_2NCF_2COOH + HF$$

The formation of esters by the reaction of fully fluorinated 2-nitroalkyl nitrites with alcohols proceeds similarly:

$$O_2NCF_2CF_2ONO + ROH \rightarrow O_2NCF_2CF_2OH + RONO$$

$$O_2NCF_2CF_2OH \rightarrow O_2NCF_2COF + HF \xrightarrow{ROH} O_2NCF_2COOR + HF.$$

The reactions of tetrafluoro-2-nitroethyl nitrite with acids are very similar to this in type, which is an indirect proof of the correctness of the proposed reaction mechanism.

When it reacts with strong acids, such as sulfuric or chlorosulfonic acid, tetrafluoro-2-nitroethyl nitrite is converted quantitatively into difluoronitroacetyl fluoride. Reaction proceeds, as in the case of hydrolysis, with elimination of NO, which is then replaced by hydrogen from the acid:

$$O_2NCF_2CF_2ONO + H_2SO_4 \rightarrow [\underline{O_2NCF_2CF_2OH}] + NOOSO_3H$$

$$\downarrow$$

$$O_2NCF_2-\overset{\overset{O}{\|}}{C}-F$$

The resulting tetrafluoro-2-nitroethanol spontaneously loses hydrogen fluoride with formation of difluoronitroacetyl fluoride. Only the acid fluoride is obtained because the necessary elements for hydrolysis to difluoronitroacetic acid are not present in the reaction medium. With weaker acids the formation of the acid fluoride from the nitro nitrite occurs in lower yield; with acetic acid the reaction does not occur at all.

As would be expected, the pyrolysis of fully fluorinated 2-nitroalkyl nitrites proceeds by a homolytic mechanism. When tetrafluoro-2-nitroethyl nitrite vapor is heated to 250°, the weakest bond breaks with formation of NO and $O_2NCF_2CF_2O$ radicals:

$$O_2NCF_2CF_2O-NO \xrightarrow[Q]{} O_2NCF_2CF_2O^{\cdot} + NO$$

The radical $O_2NCF_2CF_2O$ may lose carbonyl fluoride and be converted into another radical, as in the photooxidation of perfluorohydrocarbons; or it may be stabilized by the elimination of a fluorine atom, which, by combining with NO, forms nitrosyl fluoride. As a result of such stabilization the radical $O_2NCF_2CF_2O$ is converted into difluoronitroacetyl fluoride:

$$O_2N-CF_2-\overset{\overset{O}{\|}}{C}-F$$

Under the pyrolysis conditions the acid fluoride formed is degraded further. In this case, two mechanisms can be imagined: direct elimination of nitrosyl fluoride:

$$O_2N-CF_2-\overset{\overset{O}{\|}}{C}-F \rightarrow FNO + F-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-F$$

or elimination of an NO_2 group as the first of a series of reactions which again lead to the formation of oxalyl fluoride.

Determination of dissociation constants from conductivity measurements on solutions showed that difluoronitroacetic acid is a stronger acid than trifluoroacetic acid:

$$K_c NO_2CF_2COOH = 97\,000 \cdot 10^{-5}; \quad K_c CF_3COOH = 50\,000 \cdot 10^{-5}$$
$$K_c CCl_3COOH = 21\,000 \cdot 10^{-5}; \quad K_c CH_3COOH = 1.8 \cdot 10^{-5}.$$

Hence, replacement of a fluorine atom by a nitro group almost doubles the tendency of the acid to ionize. The dissociation constant of tetrafluoro-2-nitropropionic acid is $K_C = 1875 \cdot 10^{-5}$.

Examination of the nitration of fluoroolefins and unsubstituted olefins with nitrogen dioxide leads to the conviction that the two reactions are chemically similar. In nonpolar solvents and in the gas phase both reactions proceed by a free-radical mechanism. This is confirmed by the conditions required to bring about these reactions and by the formation of cetain main products and by-products which, in the case of the fluoroolefins, can be isolated. The analogous products from the nitration of unsubstituted olefins undergo degradation and isomerization (alkyl nitrites in the gas phase and nitro nitroso compounds).

Formation of nitro nitrates in the nitration of olefins is generally attributed to oxidation of the nitro nitrites formed in the first place. The results obtained in the study of the nitration of fluoroolefins indicate the possibility of an indirect mechanism for the oxidation of nitro nitrites, namely decomposition into an alkoxy radical and nitric oxide followed by combination of the alkoxy radical with NO_2:

$$R - O - NO \rightarrow RO^{\cdot} + NO$$
$$RO^{\cdot} + NO_2 \rightarrow RONO_2$$

As we have shown in the cases of hexafluoro-2-nitropropyl and pentafluoro-2-nitro-2-(trifluoromethyl)propyl nitrites, the direct oxidation of nitro nitrites with gaseous oxygen is an energetically unfavorable reaction that is difficult to bring about. The main part played by the addition of oxygen in the nitration of ordinary olefins (discussed by Levy and Scaife [11]) probably consists in the regeneration of nitrogen dioxide from nitric oxide:

$$2NO + O_2 \rightarrow 2NO_2 ,$$
$$NO_2CHR - CH_2O^{\cdot} + NO_2 \rightarrow O_2NCH_2 - CHR - ONO_2.$$

TABLE 2

Formula	B.p. (°C) (p in mm)	d_4^{20}	n_D^{20}	Found %		Calc. %	
				F	N	F	N
$O_2NCF_2 - COOH$	80 (31)	1.438	1,3670	22.9	8.5	21,5	7.9
$CF_3 - CF(NO_2)COOH$	119	1.638	1,3560	39.8	7.3	39.2	7,5
$(CF_3)_2C(NO_2) - COOH$	151 (40)	—	—	42.5	—	40.5	—
$CF_3CF(NO_2)CF_2ONO_2$	72–73	1.673	1.3130	43.2	10.5	44.2	10 8
$O_2N - CF(CF_3) - CONH_2$	154 (11)	—	—	39.5	14.3	40	14.7
$O_2F_2 - CF(NO_2) - COOC_2H_5$	117.5	1.412	1.3470	33.9	6,0	34.6	6.4
$O_2NCF_2 - COOCH_3$	53 (100)	1,379	1.3567	23.8	9.7	24.5	9.0
$O_2NCF_2 - COCl$	52	1.508	1.3581	24.3	8.7	23.8	8.8
$(O_2NCF_2CO)_2O$	63 (35)	1.582	1.3590	28.6	—	28.8	—
O_2NCF_2CN	27	1.401	1.3229	28.8	24.0	31.0	23.0
$(CF_3)_2C(NO_2) - COOC_2H_5$	134	1.441	1.3362	40.2	5.2	40.3	4.9
$CF_3CF(NO_2)COCl$	37	1.659	1.3502	37.0	6,31	36.3	6.68
$CF_3CF(NO_2)CON(C_2H_5)_2$	149	1.368	1.3715	31.1	11.2	30.9	11.3
$O_2N(CF_2)_4NO_2$	110 (18)	1.798	1.3410	50.4	8.5	51.8	9.6
$O_2NCF_2CF_2NO$	23–24	1.505*	1.290*	44.2	1583	44.3	15.9
O_2NCF_2COF	15	1.512**	1.302**	39.0	—	40.0	—
$CF_3 - CF(NO_2)COF$	35	1.544	1.3133	49	7.69	49.2	7.27

*d_4^0, n_D^0; **d_4^{14}, n_D^{14}.

The mechanism of the formation of nitric esters in the nitration of paraffins can be represented similarly:

$$RONO \rightarrow RO^{\cdot} + NO,$$
$$RO^{\cdot} + NO_2 \rightarrow RONO_2.$$

In the nitration of paraffins in the gas phase at high temperature, stabilization of the alkoxy radical proceeds also with liberation of formaldehyde. The new radical formed combines with NO_2 molecules and a nitro compound is obtained which contains fewer carbon atoms than the original substance:

$$R - CH_2O^{\cdot} \rightarrow CH_2O + R^{\cdot}$$
$$R^{\cdot} + {}^{\cdot}NO_2 \rightarrow R'NO_2.$$

It will be clear that in the gas-phase nitration of olefins we may again expect the formation of nitration products having fewer carbon atoms than the original olefin.

The alkoxy radical can also react with the olefin, from which it may remove a hydrogen atom and give an alcohol:

$$O_2NCRO + CHR = CH_2 \rightarrow O_2NCROH + {}^{\cdot}CR = CH_2.$$

Reaction of the vinyl radical with the NO_2 radical gives substitution nitration products and nitro alcohols. Owing to the high stability of the C–F bond, encounters between the fully fluorinated nitroalkyl radical and the original fluoroolefin do not result in the formation of substitution nitration. The results of the present investigation show that important factors determining orientation in the nitration of fluoroolefins are the stability of the intermediate radicals and also the polarity of the fluoroolefins and of the radical-like particle NO_2. Concepts concerning the polarity of radicals, first introduced by Waters [14] and then developed by Kharash [16], Weiss [17], Dolgoplosk [18], and others, and study of the role of polarity in free-radical processes undoubtedly deserve attention and are in need of further development.

LITERATURE CITED

[1] I.L. Knunyants and A.V. Fokin, Bull. Acad. Sci. USSR, div. chem. sci. 1952, 262.*

[2] I.L. Knunyants, A.M. Shchekotikhin and A.V. Fokin, Bull. Acad. Sci. USSR, div. chem. sci. 1953, 282.*

[3] I.L. Knunyants and A.V. Fokin, Bull. Acad. Sci. USSR, div. chem. sci. 1955, 705.*

[4] I.L. Knunyants and E.G. Bykhovskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1955, 852.*

[5] Coffman, J. Org. Chem. 14, 747 (1949).

[6] R.N. Haszeldine, J. Chem. Soc. 1953, 2075.

[7] H. Hass and A. Whitaker, U.S. Patent No. 2447504 (1948); C.A. 43, 3024 (1949).

[8] I.L. Knunyants and A.V. Fokin, Proc. Acad. Sci. USSR 111, 1035 (1956).*

[9] I.L. Knunyants and A.V. Fokin, Proc. Acad. Sci. USSR 112, 67 (1957).*

[10] R.N. Haszeldine and J.E. Osborn, J. Chem. Soc. 1956, 61.

[11] N. Levy and C. Scaife, J. Chem. Soc. 1946, 1093.

[12] A.I. Titov and A. Baryshnikova, Proc. Acad. Sci. USSR 91, 1099 (1953).

[13] A.I. Titov, Progr. Chem. 21, 883 (1952).

[14] J.W. Williams, J. Am. Chem. Soc. 58, 197 (1936).

[15] P. Grey, Trans. Faraday Soc. 51, 1363 (1955).

*Original Russian pagination. See C.B. Translation.

[16] M.S. Kharash et. al, J. Am. Chem. Soc. 64, 1621 (1942).

[17] J. Weiss, Trans. Faraday Soc. 36, 856 (1940).

[18] B.A. Dolgoplosk, B.A. Erusalimsky, V.A. Krol and L.M. Romanov, Questions of Chemical Kinetics, Catalysis, and Reactivity (Izd. AN SSSR, 1955), p. 810.*

Received October 9, 1957

*In Russian.

SYNTHESIS AND REACTIONS OF VINYL COMPOUNDS OF SILICON

COMMUNICATION 3. PREPARATION OF ALKYLCHLOROVINYLSILANES BY REACTION OF ACETYLENE WITH CHLOROSILANES CONTAINING SILICON-ATTACHED HYDROGEN, AND INVESTIGATION OF SOME OF THEIR PROPERTIES

M.F. Shostakovsky, D.A. Kochkin and V.L. Vinogradov

Investigation of the properties of unsaturated organosilicon compounds, in parcticular, the vinyl compounds $(CH_2 = CH)_nSiR_{4-n}$, is of interest owing to their tendency to undergo polymerization and addition reactions. We have shown previously that it is possible in principle to prepare trichlorovinylsilane $CH_2 = CHSiCl_3$ and dichlorovinylsilane $(CH_2 = CH)_2SiCl_2$ by direct synthesis: passage of vinyl chloride over a silicon-copper alloy [1]. Somewhat later we described the preparation of dichloromethylvinylsilane $CH_3(CH_2 = CH) - SiCl_2$ and dichloroethylvinylsilane $C_2H_5(CH_2 = CH) - SiCl_2$ by reaction between acetylene and the corresponding alkyldichlorosilanes in presence of platinized charcoal, platinized alumina, and palladized alumina [2]. There is also the isolated reference by Burkhard and Krieble [3] to the possibility of the addition of chlorosilane to acetylene. Patents have been published recently which also indicate the possibility of reaction between acetylene and various halosilanes containing silicon-attached hydrogen in presence of platinum supported by finely divided carbon [4], but the yields, the identity of the products, and the reaction conditions are not stated by the author. We considered it to be desirable to make a detailed study of the vinylation of alkyldihalosilanes (containing silicon-attached hydrogen). The present paper describes the preparation of alkyldichlorovinylsilanes from methyl- and ethyldichlorosilanes and acetylene under various reaction conditions.

It was found that the best vinylation conditions obtain in presence of palladium supported by alumina or calcium carbonate at 130-170°. Other vinylation catalysts that can be used are nickel, boron trifluoride etherate, and platinum supported by charcoal, alumina, calcium carbonate, or silica gel. The use of platinized charcoal, which is recommended in the patent literature [1], results in a low yield. In this case, vinylation is not free from danger: as is well known, charcoal brings about the decomposition of acetylene. As a result, some of our reaction mixtures exploded.

The reactions between acetylene and halosilanes containing silicon-attached hydrogen can be represented as follows:

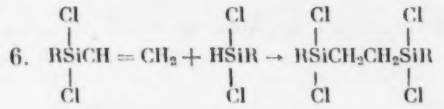
1. $RSiX_2(H) + CH \equiv CH \rightarrow RSiX_2(CH = CH_2)$, when X = halogen: Cl, Br, I, F
2. $RSiH_2X + 2CH \equiv CH \rightarrow R(CH_2 = CH)_2SiX$
3. $XSiH_3 + 3CH \equiv CH \rightarrow (CH_2 = CH)_3SiX$
4. $HSiX_3 + CH \equiv CH \rightarrow (CH_2 = CH)SiX_3$
5. $SiH_2X_2 + 2CH \equiv CH \rightarrow (CH_2 = CH)_2SiX_2$

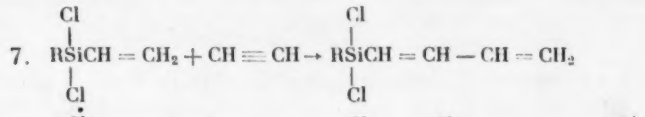
or, in a general form

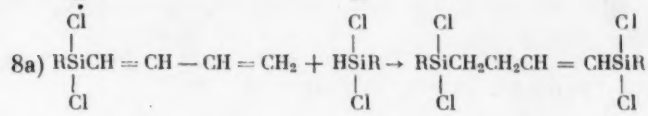
$$H_nSi(R)_{4-n} + nCH \equiv CH \rightarrow (CH_2 = CH)_nSi(R)_{4-n}$$

in which R is alkyl, aryl, or halogen and n < 4.

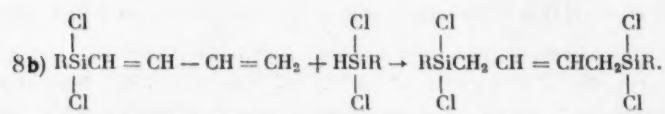
We were thus able to prepare various organosilicon compounds containing several vinyl groups. In addition, various telomeric compounds were obtained. Thus, in the vinylation of methyl- and ethyl-dichlorovinylsilanes we isolated methyl- and ethyl-butadienyldichlorosilanes $CH_3(Cl_2)SiCH = CH-CH = CH_2$ and $C_2H_5(Cl_2)SiCH = = CH-CH = CH_2$, 2,2,5,5-tetrachloro-2,5-disilahexane $CH_3(Cl_2)SiCH_2CH_2Si(Cl_2)CH_3$ and 3,3,6,6-tetrachloro-3,6-disilaoctane $C_2H_5(Cl_2)SiCH_2CH_2Si(Cl_2)C_2H_5$, and 2,2,7,7-tetrachloro-2,7-disilaoct-3-ene $CH_3(Cl_2)SiCH_2CH_2CH = = CHSi(Cl_2)CH_3$ and 3,3,8,8-tetrachloro-3,8-disiladec-4-ene $C_2H_5(Cl_2)SiCH_2CH_2CH = CHSi(Cl_2)C_2H_5$. The formation of these telomeric products can be represented as follows:







or

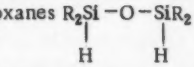
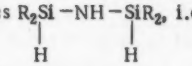


9. $R(Cl_2)SiCH_2CH_2CH = CHSi(Cl_2)R + CH \equiv CH \rightarrow$
$R(Cl_2)SiCH_2CH_2CH = C(SiCl_2R)CH = CH_2$ etc.

The structure of butadienyldichloroethylsilane was confirmed by its conversion into butyltriethylsilane [5]:

$$C_2H_5(Cl_2)SiCH=CHCH=CH_2 \xrightarrow[\text{Raney nickel}]{+H_2} C_2H_5(Cl_2)SiCH_2CH_2CH_2CH_3 \xrightarrow{+2C_2H_5MgBr} (C_2H_5)_3SiCH_2CH_2 \times CH_2CH_3.$$

Methyl- and ethyl-chlorovinylsilanes and the other compounds referred to above are mobile liquids of pungent odor, which fume in air and are readily hydrolyzed by water; they are soluble in ether, benzene, acetone and other solvents. Methyl- and ethyl-dichlorovinylsilanes can be distilled under atmospheric pressure without decomposition [2]. Methyl- and ethyl-butyldichlorosilanes, and also the tetrachlorodisilaalkenes, can be distilled unchanged only under reduced pressure. When heated, they polymerize with formation of thermoplastic resins. The high-boiling residues from the vinylation are thermoplastic solids, probably of very high molecular weight.

The starting materials for the vinylation were methyl- and ethyl-dichlorosilanes, which were obtained by direct synthesis [5]; they have now become quite accessible materials for use in synthesis. As starting materials we can recommend also various alkylsilanes of structure $R_nSi(H)_{4-n}$, in which R is alkyl, aryl, alkoxyl, or aryloxyl, and various siloxanes  and silazanes  , i.e., compounds containing a mobile hydrogen, several of which have been prepared by us [6, 7].

EXPERIMENTAL

1. Vinylation of Dichloromethylsilane. A mixture of 345 g (3 moles) of dichloromethylsilane (b.p. 41.5°; d_4^{20} 1.1047), and 1 g of palladized alumina (0.5% Pd) was prepared in a one-liter autoclave, and 60 liters of acetylene* was passed in. With constant turning the autoclave was heated to 130-170° and kept at that temperature

*Gaseous acetylene is dissolved to a considerable extent by alkyldichlorosilanes, and this makes it possible to introduce the necessary amount of acetylene.

for one and a half to two hours. The start of the reaction was marked by a fall in pressure in the autoclave. The reaction products were fractionated through a column having a metal filling (20 theoretical plates). The following compounds were isolated: 1) 69.0 g (20% by weight) of unchanged dichloromethylsilane; 2) 101.9 g (30.0%) of dichloromethylvinylsilane, b.p. 91° (742 mm); n_D^{20} 1.4270; d_4^{20} 1.0868; found MR 33.33; calculated $C_3H_6SiCl_2$ MR 33.70 [2]; 3) 18.0 g of butadienyldichloromethylsilane $CH_3(Cl_2)SiCH = CHCH = CH_2$; b.p. 43-45.5° (11.0-11.5 mm); n_D^{20} 1.444; d_4^{20} 1.0917; found MR 41.77, calculated for $C_5H_8SiCl_2$ MR 41.82.

Found %: C 35.12; 35.56; H 4.98; 4.91; Cl 42.01; 42.42; Si 16.90; 16.78. $C_5H_8(Cl)_2SiCl_2$.
Calculated %: C 35.93; H 4.82; Cl 42.44; Si 16.81.

4) 49.8 g of 2,2,5,5-tetrachloro-2,5-disilahexane $CH_3(Cl_2)SiCH_2CH_2Si(Cl_2)CH_3$, b.p. 72-73.5° (9.0 mm); n_D^{20} 1.4760; d_4^{20} 1.2628; found MR 57.1; calculated for $C_4H_{10}Si_2Cl_4$ MR 56.95.

Found %: C 19.15; 19.20; H 3.85, 3.73; Cl 54.48, 54.63; Si 21.89, 21.93. $C_4H_{10}Si_2Cl_4$.
Calculated %: C 18.74; H 3.90; Cl 55.47; Si 21.87.

5) 22.6 g of 2,2,7,7-tetrachloro-2,7-disilaoct-3-ene $CH_3(Cl_2)SiCH_2CH_2CH = CHSi(Cl_2)CH_3$; b.p. 95° (16 mm); 100° (16.5 mm); n_D^{20} 1.4765; d_4^{20} 1.1954; found MR 65.74; calculated for $C_6H_{12}Si_2Cl_4$ MR 66.76.

Found %: C 25.12, 25.20; H 4.35, 4.35; Cl 50.20, 50.75; Si 19.92; 19.82. $C_6H_{12}Si_2Cl_4$.
Calculated %: C 25.52; H 4.64; Cl 50.2; Si 19.92.

6) 60.0 g (17.7% by weight) of high-boiling products (viscous resins that softens with heat).

2. Vinylation of dichloroethylsilane. a) In presence of palladized alumina. Reaction was between 344.0 g of dichloroethylsilane (b.p. 74-76° (756 mm); n_D^{20} 1.4129; d_4^{20} 1.0849) and 65.5 liters of acetylene in presence of 1.5 g of palladized alumina (0.5% Pd). The conditions were as described above. Fractionation gave the following compounds: 1) 112.6 g of dichloroethylsilane; 2) 91.0 g (33.0% on the amount of dichloroethylsilane that reacted) of dichloroethylvinylsilane, b.p. 118.5-119.5° (756 mm); n_D^{20} 1.4385; d_4^{20} 1.0664; found MR 38.22; calculated MR 38.89 [2]; 3) 21 g $C_2H_5(Cl_2)SiCH = CH-CH = CH_2$; b.p. 47.0° (4.5 mm), 62° (11 mm), 65° (11.5 mm); n_D^{20} 1.4784; d_4^{20} 1.0783; found MR 47.16; calculated for $C_6H_{10}SiCl_2$ MR 46.46.

Found %: C 39.45, 39.49; H 5.76, 5.64; Cl 38.79, 38.64; Si 16.17, 16.39. $C_6H_{10}SiCl_2$.
Calculated %: C 39.77; H 5.57; Cl 39.1; Si 15.52.

4) 35.02 g of 3,3,6,6-tetrachloro-3,6-disilaoctane $C_2H_5(Cl_2)SiCH_2CH_2Si(Cl_2)C_2H_5$, b.p. 249-250° (754 mm); 101-102° (8 mm); n_D^{20} 1.4740; d_4^{20} 1.187. The literature gives: b.p. 249° (750 mm); n_D^{20} 1.4742; d_{25} 1.192 [3];

5) 32.0 g of 3,3,8,8-tetrachloro-3,8-disiladec-4-ene $C_2H_5(Cl_2)SiCH_2CH_2CH=CHSi(Cl_2)C_2H_5$, b.p. 119-121° (8.0 mm); n_D^{20} 1.4869; d_4^{20} 1.1910; Found MR 75.05; calculated for $C_8H_{16}Si_2Cl_4$ MR 75.00.

Found %: C 30.51, 30.39; H 5.14, 5.29; Cl 44.73, 45.05; Si 18.07, 18.12. $C_8H_{16}Si_2Cl_4$.
Calculated %: C 30.97; H 5.10; Cl 45.70; Si 18.10.

6) 40.0 g of high-boiling products (viscous resin that softens with heat).

b) In presence of palladized calcium carbonate. Reaction was between 345.0 g of dichloroethylsilane and 58.0 liters of acetylene in presence of 1.55 g of palladized calcium carbonate (0.5% Pd). The conditions were as described above. Fractionation gave: 1) 100.0 g of dichloroethylsilane; 2) 101.1 g (34.2%) of dichloroethylvinylsilane, b.p. 118.5-119.5° (756 mm); n_D^{20} 1.4385; d_4^{20} 1.0664; 3) 28.9 g of butadienyldichloroethylsilane, b.p. 74° (22 mm); n_D^{20} 1.4782; d_4^{20} 1.0790; 4) 48.9 g of 3,3,6,6-tetrachloro-3,6-disilaoctane; 5) 42.0 g of 3,3,8,8-tetrachloro-3,8-disiladec-4-ene $C_2H_5(Cl_2)SiCH_2CH_2CH = CHSi(Cl_2)C_2H_5$; b.p. 120° (8.5 mm); n_D^{20} 1.4855; d_4^{20} 1.1910; and 6) 65.0 g of high-boiling products.

3. Ethylation of $C_2H_5(Cl_2)SiCH = CH-CH = CH_2$. Butadienyldichloroethylsilane (18.0 g, i.e., 0.1 mole), as a solution in 20 ml of ether, was hydrogenated at room temperature over Raney nickel until hydrogen ceased to be absorbed. About 4.3 liters of hydrogen was absorbed (theoretical amount 4.48 liters). The reaction products

were vacuum-fractionated, and 9.6 g of butyldichloroethylsilane was isolated and was ethylated with excess of ethylmagnesium bromide in ether. The reaction mixture was treated with water, and the ether layer was separated and dried over potassium carbonate. Fractionation gave 4.5 g of a substance of b.p. 189.0° (748 mm); n_D^{20} 1.4330; d_4^{20} 0.7750, which corresponded to butyltriethylsilane. For $C_{10}H_{24}Si$ the literature gives: b.p. 190.5-191.5° (760 mm); $n_D^{25.4}$ 1.4322; $d_4^{25.4}$ 0.7742 [8].

The method given here is suitable for the vinylation of halosilanes of structure H_nSiX_{4-n}, e.g., $HSiCl_3$, H_2SiCl_2, $HSiCl_3$.

SUMMARY

1. The vinylation of alkyl (or aryl) halosilanes by treatment with acetylene was investigated.

2. Apart from methyl- and ethyl-dichlorovinylsilanes [2], the following compounds were isolated from the reaction products: methyl- and ethyl-butadienyldichlorosilanes, 2,2,5,5-tetrachloro-2,5-disilahexane and 3,3,6,6-tetrachloro-3,6-disilaoctane, and also 2,2,7,7-tetrachloro-2,7-disilaoct-3-ene and 3,3,8,8-tetrachloro-3,8-disiladec-4-ene.

3. Catalysts of the platinum-palladium group (metals, acids, and salts) are effective in the vinylation reaction.

4. Vinylation can be carried out batchwise in an autoclave or continuously in an apparatus similar to that used for the vinylation of alcohols.

LITERATURE CITED

[1] M.F. Shostakovsky and D.A. Kochkin, Bull. Acad. Sci. USSR, div. chem. sci. 1954, 174.*

[2] M.F. Shostakovsky and D.A. Kochkin, Proc. Acad. Sci. USSR 109, 113 (1956);* M.F. Shostakovsky, K.A. Andrianov, D.A. Kochkin and V.L. Vinogradov, Authors' Certificate (1956).

[3] C.A. Burkhard and K.H. Krieble, J. Am. Chem. Soc. 69, 2687 (1947).

[4] G.H. Wagner, U.S. Patent 2637738 (1953); C.A. 48, 8254 (1954).

[5] K.A. Andrianov and D.A. Kochkin, Authors' Certificate No. 71050 (1947); Bull. Inventions 4,16 (1948); Authors' Certificate No. 9517 (1949).

[6] M.F. Shostakovsky, D.A. Kochkin and V.M. Rogov, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1062.*

[7] M.F. Shostakovsky, D.A. Kochkin, V.L. Vinogradov and V.A. Neterman, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1269.*

[8] A. Rygden, Z. Phys. Chem. 90, 243 (1915).

[9] M.F. Shostakovsky and D.A. Kochkin, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1151.*

Received July 22, 1956

N.D. Zelinsky Institute of Organic Chemistry of the
Academy of Sciences, USSR

*Original Russian pagination. See C.B. translation.

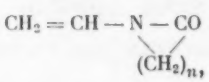
INVESTIGATION OF LACTONES AND LACTAMS

COMMUNICATION 9. SYNTHESIS OF N-VINYL LACTAMS AND SOME OF THEIR PROPERTIES

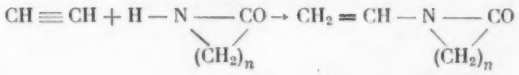
M.F. Shostakovsky, F.P. Sidelkovskaya and M.G. Zelenskaya

Much attention has recently been given in the literature to the synthesis and polymerization of nitrogen-containing vinyl compounds. Among the methods of preparing these, that proposed by Favorsky and Shostakovsky (direct vinylation, carried out in the first place on alcohols and phenols [1]) is of considerable importance. The further development of this reaction led to the synthesis of many valuable compounds and forms an example of the joint effect of Russian (Favorsky) and foreign (Reppe) work on the successful development of an important field of organic chemistry.

Among vinyl compounds in which there is a nitrogen-attached vinyl group, N-vinyl lactams occupy a special place:

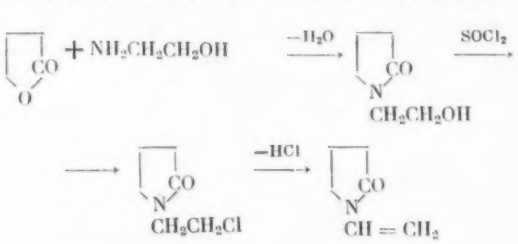


i.e., 1-vinyl-2-pyrrolidinone (n = 3), 1-vinyl-2-piperidone (n = 4),* and 2-oxo-1-vinylhexamethyleneimine [N-vinylcaprolactam] (n = 5). These substances can be obtained by reaction between acetylene and the corresponding lactams:



(I)

We previously described the synthesis of N-vinylcaprolactam from acetylene and caprolactam; the reaction was carried out in a solvent (toluene, butyl vinyl ether, gasoline), and the potassium or sodium salt of the lactam was used as catalyst [3, 4]. In foreign literature we meet mainly N-vinyl-2-pyrrolidinone, because its polymers find extensive application in medicine, cosmetics, the textile industry, and other fields [5, 6]. There is also a brief reference to the synthesis of 1-vinyl-2-piperidone [7]. 1-Vinyl-2-pyrrolidinone is generally prepared by the vinylation of 2-pyrrolidinone, but only very general information is available on how this reaction is carried out. It has been recently proposed to synthesize N-vinyl-2-pyrrolidone from butyrolactam and 2-aminoethanol [8]:

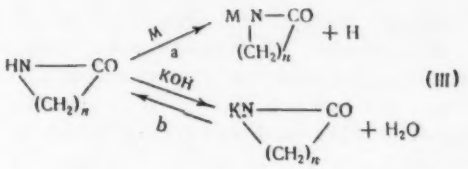


*Preceding eight communications, see [2-4, 10, 12, 13, 15].

The second method is of less interest, for there are more stages and intermediate products. According to patents [5], the vinylation of 2-pyrrolidinone has been carried out both in presence and in absence of solvents; hydroxides, alkoxides, and metal derivatives of lactams have been recommended as catalysts. Of the chemical properties of 1-vinyl-2-pyrrolidinone, only its polymerization has been described in the literature.

We here describe a detailed investigation of the vinylation of lactams and some reactions of the resulting N-vinyl lactams. The experiments were carried out with pyrrolidinone and piperidine. The caprolactam used was the commercial product. 2-Piperidone was prepared by the Laboratory for Heteroorganic Synthesis and made available for our use.* For the preparation of 1-vinyl-2-pyrrolidone the necessary pyrrolidone was synthesized by the condensation of butyrolactone with ammonia according to Späth's method [17]. It was shown that the choice of catalysts and solvents is of great importance for the successful performance of the vinylation reaction.

As will be seen from Table 1, alkali-metal derivatives of lactams are general and highly effective catalysts for the vinylation of lactams. These are readily prepared by direct reaction between the lactam and sodium or potassium (Equation IIIa); potassium is less suitable owing to its tendency to catch fire.



(III)

The yield of vinylation product is almost the same for the two alkali-metal derivatives and varies in different cases from 50 to 70%.

It was of interest also to determine whether catalysts such as KOH can be used for the synthesis of N-vinyl lactams, for these are the most widely used catalysts in reactions of this sort. In previous papers [3, 4] it was stated that it was not found possible to synthesize N-vinylcaprolactam in presence of potassium hydroxide. Detailed investigation showed that the water liberated in the reaction of KOH with caprolactam has an unfavorable effect on the vinylation process. The presence of water either favors the decomposition of the lactam salt (Equation IIIb) at the temperature of the reaction, or it has a direct effect on the normal course of the reaction. In this case, therefore, the usual method, in which KOH and the compound to be vinylated are loaded together into the autoclave, cannot be used. It is necessary first to heat the lactam with KOH and remove the water formed; only then can the mixture be used as a catalyst. Removal of water was effected by azeotropic distillation, for which benzene, toluene, etc. can be used; removal of water with the vapor of the original lactam was found to be more effective. It should be noted that even this method does not give the same result for all lactams. The highest yield of N-vinyl lactam obtained with catalyst prepared from KOH was attained in the case of 1-vinyl-2-pyrrolidinone, and the lowest in the case of 1-vinyl-2-piperidone (Table 1).

Another very important question is the choice of solvent for the vinylation medium. As already stated [4], the vinylation of N-vinylcaprolactam was carried out in media of toluene, butyl vinyl ether, gasoline, and butyl alcohol. A drawback of these solvents is their low solvent power for acetylene, so that it is necessary to introduce several fresh portions of acetylene until absorption is complete. Shostakovsky, Prilezhaeva and Tsymbal [9] have recently suggested the use of dioxane for the vinylation of methyl α-glucoside; this is a good solvent for acetylene and it is therefore possible to carry out the reaction in presence of excess of acetylene. Our experiments showed that in the vinylation of lactams the use of dioxane again makes repeated introduction of acetylene unnecessary and considerably accelerates the process. The vinylation of 0.7-0.9 mole of lactam requires 10-12 hours instead of the usual 24-25 hours.

With the exception of 1-vinyl-2-pyrrolidinone, the N-vinyl lactams obtained are low-melting crystalline solids; they are hygroscopic and soluble in water (1-vinyl-2-pyrrolidinone is the most soluble, and N-vinylcaprolactam is the least). Qualitative reactions given by these compounds are: 1) slow appearance of a lilac coloration with Schiff's reagent; and 2) the formation of iodoform by the action of alkali and iodine. The second reaction is used not only qualitatively, but also for the quantitative analysis of N-vinyl lactam [10].

*We express our thanks to R. Kh. Freidlina for providing us with 2-piperidone.

TABLE 1

Effect of the Method of Preparing the Catalyst on the Yield of N-Vinyl Lactam

No.	N-Vinyl lactam	Yield of N-vinyl lactam (%)		
		catalyst prepared from lactam and Na	catalyst prepared by heating lactam with KOH	
			water removed by distillation with original lactam	water removed by distillation with toluene
1	1-Vinyl-2-pyrrolidinone	60	52	33
2	N-Vinylcaprolactam	70	24	9
3	1-Vinyl-2-piperidone	50	12	5

N-vinyl lactams are highly reactive substances and can take part both in ionic reactions and also in free-radical reactions. Comparison of the properties of N-vinyl lactams with those of vinyl ethers, which were studied in detail by Shostakovsky and co-workers [11], shows that N-vinyl lactams are less readily activated by ionic agents [12, 13], but react more readily by a free radical mechanism. When they react with water in presence of acids they are hydrolyzed with formation of acetaldehyde and the unsubstituted lactam [12]:

$$CH_2=CH-N(-(CH_2)_n-)-CO + HOH \xrightarrow{H^+} CH_3CHO + HN(-(CH_2)_n-)-CO$$

With respect to rate of hydrolysis the N-vinyl lactams may be arranged in the following order:

N-vinylcaprolactam > 1-vinyl-2-pyrrolidinone > 1-vinyl-2-piperidone

Taking N-vinylcaprolactam as our example, we showed that, in presence of acid catalysts, alcohols add to N-vinyl lactams with formation of N-(1-alkoxyethyl) lactams in low yield [13]. This reaction proceeds much less readily than in the case of vinyl ethers.

The polymerization of N-vinyl lactams is of special interest. The resulting polymers are soluble not only in most organic solvents, but also in water. In the last case colloidal solutions are formed. The literature describes the mass polymerization of 1-vinyl-2-pyrrolidinone [6] and of 1-vinyl-2-piperidone and N-vinylcaprolactam [3, 4, 14] in presence of hydrogen peroxide. In the case of 1-vinyl-2-pyrrolidinone, polymerization in aqueous solutions has also been studied [6].

In the present investigation some comparative experiments on the polymerization of 1-vinyl-2-pyrrolidinone and N-vinylcaprolactam in an aqueous medium were carried out (Table 5). It will be seen from Table 5 that 1-vinyl-2-pyrrolidinone polymerizes more readily than N-vinylcaprolactam. Thus, in Experiment 1, the yield of poly(vinylpyrrolidinone) was 92%, whereas the polymerization of N-vinylcaprolactam with the same amount of initiator and for the same time (Experiment 4) gave only 45% of polymer. Moreover, as already shown, active polymerization of N-vinylcaprolactam proceeds only above 100° (for 1-vinyl-2-pyrrolidinone, 50-60° is adequate); at lower temperatures hydrolysis occurs [15].

Further investigation showed that N-vinyl lactams do not form polymers in presence of benzoyl peroxide at 50-60° (the most characteristic temperature for this initiator), but polymerize readily in presence of free-radical catalysts of the type of 2,2'-azobis[2-methylpropionitrile] (Table 2). Breitenbach and Schmidt [16] give some kinetic data on the polymerization of 1-vinyl-2-pyrrolidinone in presence of this initiator, but the information given is incomplete; thus, there are no indications of the yields of polymer.

For the case of 1-vinyl-2-pyrrolidinone we showed that reduction in the amount of the azo nitrile results in increase in the relative viscosity of the polymer formed (Table 6). N-vinyl lactams undergo not only homopolymerization, but also copolymerization with other unsaturated compounds (methyl methacrylate, vinyl sulfides, and alkyl vinyl ethers).

TABLE 2

Polymerization of N-Vinyl Lactams in Presence of 2,2'-Azobis[2-methylpropionitrile] (0.2% on weight of monomer)

No.	N-Vinyl lactam	Temperature (°C)	Duration (hours)	Yield of polymer (%)	Relative viscosity (3% aqueous solution)
1	1-Vinyl-2-pyrrolidinone	80	24	46	2.57
2	N-Vinylcaprolactam	60	36	50	1.00
3	1-Vinyl-2-piperidone	60	36	79.6	1.21

EXPERIMENTAL

1. Synthesis of 2-pyrrolidinone. A mixture of 258 g (3 moles) of butyrolactone and 180 ml (5 moles) of liquid ammonia was prepared in a 2.5-liter rotating steel autoclave and heated at 200-220° for 15 hours (maximum pressure 40-50 atmos). Unchanged ammonia was absorbed with water. The mixture was distilled at 60-80 mm to remove ammonia and water present (50 g of water was separated). The residue was distilled at a still lower pressure; this gave 221.0 g (87.7%) of 2-pyrrolidinone, b.p. 120-124° (10.5-11 mm), and 20.5 g of resinous residue. When cool the pyrrolidinone formed clear crystals, m.p. 22-24°. The literature [17] gives b.p. 100-105° (1 mm) and m.p. 23-24°.

Vinylation of Lactams

1. Preparation of Catalyst

a) From lactams and potassium hydroxide. A solution of 20 g of the lactam in 40 ml of toluene and 5-7 g of potassium hydroxide powder were mixed in a flask fitted with a column and heated in an oil bath in such a way that an azeotropic mixture of toluene and water distilled off slowly. Heating was for four to five hours and the bath temperature was 110-160°. In those cases in which water was driven over with the lactam, 60 g of the lactam and 5-7 g of KOH were placed in the distillation flask and 40-45 g of lactam was distilled off under reduced pressure (20-25 mm).

b) From lactam and sodium. Dry dioxane (35 ml) was added to a stable emulsion of sodium prepared by dispersing the metal (2-2.5 g) in xylene (10 ml) in presence of a stabilizer. The lactam (20 g) was then added dropwise with stirring; reaction was exothermic and was complete in three to four minutes.

2. Vinylation

The catalyst obtained by (a) or (b), 80 g of the lactam, and 100 ml of dry dioxane were placed in a 2.5-liter autoclave, and under a pressure of 17-18 atmos, 17-18 liters of acetylene (approximately a threefold excess) was passed in. The mixture was heated for ten hours (at 110-125° for N-vinylcaprolactam and at 150-160° for 1-vinyl-2-pyrrolidinone and 1-vinyl-2-piperidone). The reaction product was extracted with dry ether (about 1 liter), solvent was removed from the ether extracts, and the residue was vacuum-distilled. The vinylation of lactams was carried out also in a toluene medium (the yields were substantially the same). In this case the procedure differed in that generally not more than 8-9 liters of acetylene was passed into the autoclave containing catalyst, lactam, and solvent, the mixture was heated until absorption was complete and then cooled, and acetylene was again passed in and the mixture was again heated. This procedure was continued until no further appreciable absorption of acetylene occurred. The constants of the N-vinyl lactams obtained are given in Table 3; the yields are given in Table 1.

Hydrolysis of N-Vinyl Lactams

Hydrolysis was carried out in presence of sulfuric acid. The reaction conditions required for N-vinylcaprolactam and 1-vinyl-2-pyrrolidinone were studied previously [10]. We now give data on the hydrolysis of 1-vinyl-2-piperidone. A weighed amount of 1-vinyl-2-piperidone (0.1-0.2 g), 20 ml of sulfuric acid of the required con-

TABLE 3

Constants of N-Vinyl Lactams Obtained

No.	N-Vinyl lactam	B.p. in °C (p in mm)	M.p. (°C)	n_D^t	d_4^t	MR found	MR calc.	Data in literature
1	1-Vinyl-2-pyrrolidinone	65—66 (1—1.5) 71—72 (2.5) 75—76 (3)	—	n^{20} 1.5117	d^{20} 1.0458	31.86	31.29	94—96° (13—14 mm) [5] n_D^{25} 1.5120
2	1-Vinyl-2-piperidone	94—94.5 (6.5)	45 (in sealed capillary)	—	—	—	—	B.p. 125—126° (25 mm) B.p. 42—48° [7]
3	N-Vinylcaprolactam	95—95.5 (4) 129—130 (20.5)	34—35	n^{20} 1.5133 n^{40} 1.5051	d^{20} 1.0287 d^{40} 1.0084	40.89	40.43	B.p. 125—128 (21 mm) [5]

centration, and 25 ml of 0.2 N sodium bisulfite solution were placed in a conical flask fitted with a ground stopper, and the mixture was kept in a thermostat for a definite period of time. The unchanged sodium bisulfite was titrated with 0.1 N iodine. A control experiment was carried out under analogous conditions. The results are given in Table 4.

Polymerization of 1-Vinyl-2-pyrrolidinone and N-Vinylcaprolactam in Aqueous Solutions

A 33% aqueous solution of the N-vinyl lactam, the required amount of hydrogen peroxide, and aqueous ammonia were placed in a flask fitted with a stirrer. The reaction mixture was heated in a water bath. When the mixture was cooled, water was distilled off under reduced pressure (30-40 mm) and the polymer was reprecipitated with ether from alcoholic solution and vacuum-dried to constant weight. The results are given in Table 5.

Polymerization of N-Vinyl Lactams in Presence of 2,2'-Azobis[2-methylpropionitrile]

We shall describe a typical experiment. An ampoule containing 4.75 g of freshly distilled 1-vinyl-2-pyrrolidinone and 0.0478 g of the dinitrile was placed in a thermostat at 79-81° and kept there for 24 hours. The resulting polymer was dissolved in 6 ml of dry ethanol, precipitated with 50 ml of dry ether, separated from solvents, washed four times with ether, and vacuum-dried to constant weight; yield 56.3%; relative viscosity of a 3% aqueous solution at 25°, 2.419. From the ether-alcohol solution remaining after the separation of polymer, 1.45 g of monomer and 0.28 g of resinous residue were isolated. The other polymerization experiments were carried out similarly. The results are given in Table 6.

Copolymerization of 1-Vinyl-2-piperidone with Methyl Methacrylate

Copolymerization was for 36 hours at 60° in presence of 0.2% of 2,2'-azobis[2-methylpropionitrile]; the mixtures were heated in ampoules. The copolymers which were solids, were precipitated twice from benzene solution (15 ml) with petroleum ether (150 ml) The main results are given in Table 7.

SUMMARY

1. The vinylation of lactams was studied, the examples taken being the vinylation of 2-pyrrolidinone, 2-piperidone, and caprolactam. Alkali-metal salts of the lactams were used as catalysts. It was found that

TABLE 4

Results of the Quantitative Determination of 1-Vinyl-2-Piperidone by the Hydrolysis Method (titration of sodium bisulfite)

Experiment No.	Concentration of H_2SO_4 (%)	Hydrolysis conditions		1-vinyl-2-piperidone found (%)
		temperature (°C)	duration (minutes)	
1	2	23-25	30	69.9; 69.9
2	2	40-42	30	89.8; 93.2
3	5	23-25	30	78.4; 80.2
4	5	40-42	30	94; 94.4
5	10	23-25	30	81.2; 85.1
6	10	40-42	30	95.9; 97.4
7	10	40-42	60	98.7; 99.9

TABLE 5

Polymerization of 33% Aqueous Solutions of N-Vinyl Lactams (initiator H_2O_2, activator NH_3 (0.3% on monomer taken))

No.	N-Vinyl lactam	Amount of monomer taken (g)	Amount of H_2O_2 (% on monomer)	Reaction temperature (°C)	Duration of reaction (hours)	Yield of polymer (%)	Relative viscosity of 3% aqueous solutions at 25°
1	1-Vinyl-2-pyrrolidinone	40	1.7	50-60	5	92.1	2.811
2	"	20	2.1	50-60	2	77.2	2.431
3	"	40	3.1	50-60	3	95	1.582
4	N-Vinylcaprolactam	10	1.7	101-102*	6	45.5	1.400
5	"	10	2.3	99-101*	6	50.0	1.465
6	"	10	2.7	101-102*	6	40.0	1.322

*In these experiments the temperatures of the reaction mixtures were nearly the same, but the temperatures in the external baths varied by 25° (127-130° in Experiment 5 and 153-155° in Experiments 4 and 6).

TABLE 6

Polymerization of 1-Vinyl-2-pyrrolidinone (Catalyst 2,2'-azobis[2-methylpropionitrile], temperature 80°, duration 24 hours)

Experiment No.	Amount of catalyst (% on monomer taken)	Yield of polymer (%)	Amount of polymer isolated (%)	Relative viscosity of 3% solution of polymer
1	1	56.3	31.4	2.419
2	0.2	45.9	40.8	2.570
3	0.1	48.7	41.3	3.001
4	0.05	46.6	45.8	3.194

TABLE 7

Results of the Copolymerization of 1-Vinyl-2-piperidone (VP) with Methyl Methacrylate (MM)

Amount taken (moles %)		Yield (%)	Relative viscosity*	Nitrogen content of copolymer (%)	Number of monomer units (moles%)	
VP	MM				VP	MM
				1.96	14.8	85.2
30	70	83.3	1.74	2.00		
50	50	70.2	–	4.16	30.7	69.3
				3.97		

*The relative viscosity was measured at 20° on solutions containing 1 g of polymer in 100 ml of benzene.

the most convenient method of preparing these salts is direct reaction between the lactams and alkali metals. It was shown that water has an unfavorable effect on the course of the vinylation.

2. It was shown that, like other N-vinyl lactams, 1-vinyl-2-piperidone is hydrolyzed in an acid medium; optimum hydrolysis conditions were determined.

3. The polymerization of N-vinyl lactams was carried out in presence of 2,2'-azobis[2-methylpropionitrile], and also in presence of hydrogen peroxide in aqueous solution. The copolymerization of 1-vinyl-2-piperidone with methyl methacrylate was carried out.

LITERATURE CITED

[1] A.E. Favorsky and M.F. Shostakovsky, J. Gen. Chem. 13, 1 (1948).

[2] M.F. Shostakovsky, F.P. Sidelkovskaya and M.G. Zelenskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1957, 1406*; J. Appl. Chem. 30, 324 (1957).*

[3] M.F. Shostakovsky, N.A. Medzykhovskaya and M.G. Zelenskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1952, 632.*

[4] M.F. Shostakovsky, F.P. Sidelkovskaya and M.G. Zelenskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1952, 690.*

[5] French Patent 865354; C. 1941, 2, 2735; U.S. Patent 2317804, 1943; C.A. 1943, 6057.

[6] W. Reppe, Polyvinil Pyrolidon (Berlin, 1954).

[7] R.I. Longley and W.S. Emerson, J. Am. Chem. Soc. 74, 2012 (1952).

[8] B. Puetzer, L. Katz and L. Horwitz, J. Am. Chem. Soc. 74, 4959 (1952).

[9] M.F. Shostakovsky, E.N. Prilezhaeva and L.V. Tsymbal, Proc. Acad. Sci. USSR 99 (1954).

[10] M.F. Shostakovsky, F.P. Sidelkovskaya and M.G. Zelenskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 615.*

[11] M.F. Shostakovsky, Vinyl Esters (Izd. AN SSSR, Moscow, 1952).**

[12] M.F. Shostakovsky, F.P. Sidelkovskaya and M.G. Zelenskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1954, 689.*

[13] M.F. Shostakovsky and F.P. Sidelkovskaya, J. Gen. Chem. 24, 1576 (1954).*

[14] M.F. Shostakovsky, F.P. Sidelkovskaya, M.G. Zelenskaya and E.S. Morgunova, All-Union Chem. Soc. No. 3, 5 (1955).

[15] M.F. Shostakovsky and F.P. Sidelkovskaya, Bull. Acad. Sci. USSR, div. chem. sci. 1953, 108.*

*Original Russian pagination. See C.B. translation.

**In Russian.

[16] I.W. Breitenbach and A. Schmidt, Monats. 83, 833 (1952).

[17] E. Späth and S. Lintner, Ber. 69, 2728 (1936).

Received July 3, 1956

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

COPOLYMERIZATION OF BUTADIENE WITH VINYL FORMATE

S.N. Ushakov and S.S. Ivanov

The copolymerization of butadiene with vinyl esters is of interest because of the possibilities that it affords for the modification of the properties of butadiene polymer. However, owing to the very low rate of copolymerization in a hydrocarbon medium and the possibility of hydrolysis in emulsions, the preparation of copolymers of butadiene with vinyl esters was considered impossible until recently. The copolymerization of butadiene with vinyl formate is of particular interest: the readiness with which vinyl formate is hydrolyzed when incorporated in a polymer chain [1] gives grounds for supposing that a copolymer of butadiene and vinyl formate would be readily hydrolyzed with formation of a rubber-like product having free hydroxy groups, the content of which would have a certain effect on the physicomechanical properties of the polymer. In the present investigation an attempt was made to copolymerize butadiene with vinyl formate in the mass with the aid of an oxidation-reduction system.

There is very little information in the literature on polymerization in a homogeneous hydrocarbon medium in presence of oxidation-reduction systems. Kern [2] showed that metal salts accelerate the polymerization of unsaturated compounds in presence of benzoyl peroxide and of benzoin and other reducing agents. Medvedev and co-workers [3] noted the acceleration of polymerization initiated by peroxides by the presence of certain amines and ketones. Dolgoplosk, Tinyakova and Rabinovich [4] showed that an oxidation-reduction system consisting of cumene hydroperoxide, dihydroxymaleic acid, and iron naphthenate can be used for polymerization in a homogeneous hydrocarbon medium. Wall [5] showed that a very active system for use in polymerization is one consisting of peroxides and iron salts in combination with carbohydrates.

EXPERIMENTAL

Butadiene was first purified from butenes with the aid of cuprous chloride [6, 7], distillation, and passage through a system consisting of wash bottles containing 10% sulfuric acid and distilled water and of potassium hydroxide and calcium chloride columns. Vinyl formate was synthesized by the liquid-phase method [8]. The monomer had a constant boiling point of 46° (with variations of ~0.1°); d_4^{20} 0.9582; n_D^{20} 1.3845; monomer content 99.9%; before use the monomer was distilled off from the inhibitor (hydroquinone). The system used in the copolymerization contained cumene hydroperoxide (0.3%), dihydroxymaleic acid with two molecules of water of crystallization (0.3%), and ferrous naphthenate (0.2 mole per mole of cumene hydroperoxide).

The cumene hydroperoxide preparation contained 77% of the pure substance; its activity (expressed as content of the pure hydroperoxide) was checked by iodometric titration. Ferrous naphthenate, which was selected because of its high solubility in hydrocarbons, was prepared from the naphthenic acids of naphtha soap (molecular weight 200-205). Dihydroxymaleic acid and its diethyl ester were synthesized by the oxidation of tartaric acid with hydrogen peroxide [9-12].

The monomers were copolymerized in the mass. The purified and freshly distilled monomers were placed in ampoules of various sizes (10-120 ml). Dihydroxymaleic acid (DHMA) or benzoin (0.3%) was introduced into dry specially cleaned ampoules (washed with chromic acid mixture and blown out with steam). The ampoule was then cooled with solid carbon dioxide and the calculated amount of butadiene was introduced. The ampoule was again weighed and, with a fine glass rod with a groove at its end, a weighed amount of ferrous naphthenate was added. After the addition of vinyl formate, a weighed amount of cumene hydroperoxide was added by means of a pipet with a long capillary tip. The ampoules were sealed while still cool and were then placed in protective metal jackets ready for the copolymerization.

TABLE 1

Compositions of Copolymers of Butadiene (M_1) with Vinyl Formate (M_2)

Polymerization initiator	Temperature (°C)	$M_1 : M_2$	Duration of copolymerization (hours)	Yield (%)	Analysis of copolymer (%)			Composition of copolymer (moles %)				Unchanged monomer (moles %)		Mole fraction m_2 in copolymer	Mole fraction M_2 in monomer mixture
					C	H	O	combustion analysis		hydrolysis (0.1 N NaOH)					
								m_1	m_2	m_1	m_2	M_1	M_2		
Benzoyl peroxide (0.2%)	120	1 : 1	400	17.4	84.9	11.0	4.1	92.0	8.0	91.0	9.0	34.0	48.6	0.08	0.7
Cumene hydroperoxide (0.3%) + benzoin (0.3%) + ferrous naphthenate (0.2 mole per mole of hydroperoxide)	120	1 : 1	300	10.9	79.45	11 07	9.48	80.5	19.5	—	—	41.2	47.8	0.195	0.5
		1 : 4	300	Did not polymerize				—	—	—	—	—	—	—	0.8
		4 : 1	72	7.4	83.16	11.02	5.82	88.5	11.5	—	—	73.5	19.2	0.115	0.2
DHMA (0.3%) + cumene hydroperoxide (0.3%) + ferrous naphthenate (0.2 mole per mole of hydroperoxide)	65	4 : 1	300	16.2	83.1	11.0	5.9	88.3	11:7	86.9	13.1	65.7	18.1	0.117	0.2
	85	4 : 1	140	12.0	81.5	11.1	7.4	84.8	15.2	84.0	16.0	69.8	18.2	0.152	0.2
	85	1 : 1	150	9.7	82.6	10.9	6.5	87.4	12.6	87.0	13.0	41.5	48 8	0.126	0.5
DHMA diethyl ester (0.3%) + cumene hydroperoxide (0.3%) + ferrous naphthenate (0.2 mole per mole of hydroperoxide)	85	1 : 1	100	10.1	79.8	10.7	9.5	81.1	18.9	80.7	19.3	41.8	48.1	0.189	0.5

TABLE 2

Compositions and Intrinsic Viscosities of Copolymers Obtained in Presence of the Oxidation-Reduction System Dihydroxymaleic Acid + Cumene Hydroperoxide + Ferrous Naphthenate

Composition of oxidation-reduction system	Temp. (°C)	M_1:M_2	Duration of copolymerization (hours)	Yield (%)	Analysis of copolymer (%)			Composition of copolymer (moles%)				Unchanged monomer (moles %)		Intrinsic viscosity [η]
					C	H	O	combustion analysis		hydrolysis with 0.1 N NaOH				
								m_1	m_2	m_1	m_2	M_1	M_2	
Dihydroxymaleic acid + cumene hydroperoxide + ferrous naphthenate	120	1:1	50	11.0	83.2	10.8	6.0	88.8	11.2	88.6	11.4	40.2	48.7	1.63
	120	2:1	50	18.5	84.6	11.0	4.4	91.5	8.3	92.7	7.3	49.7	31.8	4.57
	120	4:1	50	16.2	84.8	11.0	4.2	91.6	8.4	93.3	6.7	65.1	18.6	3.03

TABLE 3

Comparison of the Effects of the Chemical Nature of the Radical Attached to Iron on the Composition and Intrinsic Viscosity of the Copolymer

Identity of R, attached to iron	M_1 : M_2	Duration of copolymerization (hours)	Conversion (%)	Combustion analysis of copolymer (%)			Content of monomer units in copolymer (moles %)				Intrinsic viscosity [η]
							according to combustion analysis		according to hydrolysis data		
				C	H	O	butadiene	vinyl formate	butadiene	vinyl formate	
Naphthenate	2:1	50	18.5	84.6	11.0	4.4	91.5	8.5	92.7	7.3	4.57
Stearate	2:1	50	88.2	79.1	10.8	10.1	80.1	19.9	78.2	21.8	4.10
Naphthenate	4:1	50	16.2	84.8	11.0	4.2	91.6	8.4	93.3	6.7	3.03
Stearate	4:1	50	82.0	82.9	10.7	6.4	88.0	12.0	86.8	13.2	3.10

TABLE 4

Compositions and Intrinsic Viscosities of Copolymer Fractions

Fraction No.	Analysis of copolymer (%)			Composition of copolymer (moles %)		Intrinsic viscosity [η]
	C	H	O	butadiene (M_1)	vinyl formate (M_2)	
Original copolymer	82.9	10.7	6.4	88.0	12.0	3.03
I	82.2	10.6	7.2	86.4	13.6	2.9
II	83.8	11.0	5.0	89.8	10.2	2.1
III	81.6	10.9	7.5	85.2	14.8	1.8
IV	82.8	11.0	6.2	87.6	12.4	1.3
V	83.1	10.8	6.1	88.4	11.6	0.95
VI	81.7	9.6	8.7	85.4	14.6	0.63

When 0.2% of benzoyl peroxide was used the copolymer was obtained by long heating (400 hours) of the monomer mixture at 120° in a molar ratio of butadiene (M_1) to vinyl formate (M_2) of 1:1. The copolymer was a soft creamy white elastic mass. It was readily soluble in benzene, moderately in gasoline and ether, and insoluble in acetone; it swelled in chloroform. It could be precipitated from benzene solution by methanol and ethanol. The compositions of the copolymers are given in Table 1.

When vinyl formate predominated ($M_1 : M_2 = 1 : 4$, and less) no copolymerization occurred, even at 120°. Copolymerization was rapid at $M_1 : M_2 = 4 : 1$ (72 hours) and became slower as the vinyl formate content of the original mixture diminished. At $M_1 : M_2 = 1 : 1$, the rate of copolymerization was reduced to about one-quarter (300 hours).

A more effective system was that consisting of dihydroxymaleic acid (and its diethyl ester), cumene hydroperoxide, and ferrous naphthenate. However, at room temperature in presence of this system no copolymerization of butadiene with vinyl formate was observed, even after long shaking of the monomer mixture. At 65° there was an appreciable change in viscosity, and a sticky viscous mass was formed after 100 hours. At higher temperatures (85°, 120°) the rate of copolymerization was correspondingly higher. Hence, the use of dihydroxymaleic acid and its diethyl ester instead of benzoin results in more rapid copolymerization. The maximum yield of copolymer was obtained at $M_1 : M_2 = 2 : 1$ (18.5% in 50 hours). The compositions of the copolymers are given in Tables 1 and 2.

The products were not mixtures of polyvinyl formate and polybutadiene; they were readily soluble in benzene and completely insoluble in acetone and chloroform, even after prolonged extraction at the boil. As is well known, polyvinyl formate is soluble in acetone and chloroform and insoluble in benzene. Hydrolysis of the copolymers with aqueous or alcoholic 0.1 N NaOH for ten hours at 60-80° did not result in the isolation of polyvinyl alcohol, as it would have in the case of polyvinyl formate.

The products obtained in the ampoules were always clear, viscous liquids and consisted of a homogeneous solution of copolymer in a mixture of monomers. The precipitated and dried samples of copolymers were slightly yellowish or brownish-white elastic rubber-like masses.

The intrinsic viscosities in benzene solution (Table 2) show that the molecular weights of the copolymers were fairly high. The highest intrinsic viscosity was possessed by the copolymer obtained at $M_1 : M_2 = 2 : 1$.

It was found that, in spite of the low solubility of iron stearate in the monomer mixture, the use of this substance instead of the naphthenate led to much more rapid copolymerization, and correspondingly the yield of copolymer rose from 16.2% to 88.2% (Table 3).

There was also some increase in the vinyl formate content of the copolymer. It must be supposed that the nature of the radical attached to iron is of definite significance in polymerization processes.

The copolymer obtained at a molar ratio of butadiene to vinyl formate of $M_1 : M_2 = 4 : 1$ at 120° in presence of dihydroxymaleic acid, cumene hydroperoxide, and iron stearate was fractionated by the method of pre-

TABLE 5

Compositions of Copolymers and Copolymerization Constants

Composition of oxidation-reduction system	Temperature (°C)	$M_1 : M_2$	Duration of copolymerization (hours)	Yield (%)	Analysis of copolymer (%)			Composition of copolymer Unchanged monomer (moles %)						Mole fraction m_2 in copolymer	Mole fraction M_2 in monomer mixture	r_1	r_2
					C	H	O	combustion analysis		hydrolysis (0.1 N NaOH)		M_1	M_2				
								m_1	m_2	m_1	m_2						
Dihydroxymaleic acid + cumene hydroperoxide + ferrous naphthenate	85	1 : 2	300	4.1	80.3	10.7	9.0	75.8	24.2	75.6	24.4	30.3	65.7	0.24	0.67	5.0 ±0.1	0.2 ±0.05
	85	1 : 1	80	5.3	81.5	11.0	7.5	85.1	14.9	83.6	16.4	45.5	49.2	0.15	0.50		
	85	1 : 4	450	3.8	68.1	8.2	23.7	53.7	46.3	53.8	46.2	17.9	78.2	0.46	0.80		
	85	1 : 9	500	2.6	60.2	7.0	32.8	35.2	64.8	35.4	64.6	9.1	88.3	0.65	0.90		
	85	2 : 1	50	4.9	82.8	6.4	10.8	87.7	12.3	87.5	12.5	62.4	32.7	0.125	0.33		
	85	4 : 1	50	5.0	83.9	11.0	5.0	89.9	10.1	89.0	11.0	75.5	19.5	0.10	0.20		
	85	9 : 1	50	3.8	86.8	5.8	7.4	95.9	4.1	95.6	4.4	86.4	9.8	0.04	0.10		
	85	29 : 1	48	5.6	87.2	5.7	7.1	96.7	3.3	96.9	3.1	91.25	3.15	0.033	0.03		

cipitation at constant temperature (20°) and stirring. The compositions and intrinsic viscosities of the fractions isolated are given in Table 4. Table 4 shows that fractionation results in the distribution of fractions according to molecular weight (the chemical compositions of the fractions are almost constant).

Copolymerization constants were determined graphically (selected-curve method) from the data in Table 5.

Monomer mixtures in eight different molar ratios were subjected to fractionation. The copolymers isolated at the initial stages of conversion were isolated and analyzed. The compositions of copolymers were calculated by the differential equation for copolymer composition developed by Mayo and Lewis [13, 14]:

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}.$$

The results were plotted on a graph showing the relation of the mole fraction of monomer units m_2 in the copolymer to the mole fraction of monomer M_2 in the monomer mixture. Optimum values of the relative activities r_1 and r_2 were selected by the method of trial and error, the theoretical curve to the equation for the composition of the copolymer being used for comparison purposes. The best values of r_1 and r_2 were assumed to be those giving a curve most closely fitting to the experimental points. The possible errors in the determination of r_1 and r_2 were estimated by comparison of values in the range over which the calculated curves were in accord with experimental data. Examination of $r_1 = K_{M_1 \cdot M_1} : K_{M_1 \cdot M_2}$ and $r_2 = K_{M_2 \cdot M_2} : K_{M_2 \cdot M_1}$ shows that butadiene adds to its own radical and to the vinyl formate radical considerably more rapidly than the vinyl formate radical adds to its own radical. The value of the product of the relative activities $r_1 \cdot r_2 = 5.0 \cdot 0.2 = 1.0$ shows that there is no alternation effect in this system.

For the preparation of a copolymer with free hydroxy groups, 15-20 g of a copolymer of butadiene and vinyl formate was dissolved in benzene and to this solution 1% of N-phenyl-2-naphthylamine was added as antioxidant. The solution was placed in a 500-ml two-necked round-bottomed flask fitted with reflux condenser, and 0.5 N alcoholic NaOH (calculated amount + 10% excess) was added. Hydrolysis was carried out for five hours in a stream of nitrogen at the boiling point of the benzene-alcohol solution. The solution was neutralized with 0.5 N HCl, and the reaction of the medium was checked with the aid of methyl red paper. As neutralization of the solution proceeded, it became more viscous. After removal of solvent, repeated washing with

TABLE 6

Mechanical Properties of Vulcanizates Obtained from Hydrolyzed Copolymers and Containing Free Hydroxy Groups

Sample No.	1	2
Free hydroxy groups (moles %) (from hydrolysis data)	3.1	2.1
Glass temperature (Marei's method [15])	−80.5	−80.0
Vulcanization time (minutes at 142°)	20	20
Breaking strength (kg/sq·cm) (unfilled vulcanizates)	135	146
Relative extension (%)	265	270
Residual extension (%)	12	12
Swelling in gasoline in 24 hours (%)	45.5	46.8
Swelling in benzene in 24 hours (%)	99.0	100.0
Swelling in gasoline/benzene (3:1) in 24 hours (%)	65.0	68.0
Frost stability index at −35° and 100% stretch	0.51	0.67

Note: Samples 1 and 2 were hydrolyzed copolymers obtained at molar ratios of butadiene to vinyl formate of 2:1 and 4:1, respectively, in presence of DHMA, iron stearate, and cumene hydroperoxide at 120°,

distilled water to remove salts completely, and vacuum drying at room temperature, an elastic rubber-like brown mass of copolymer containing hydroxy groups was obtained. The hydroxyl content of the copolymer was determined by two methods: hydrolysis of residual formic ester groups by 0.1 N NaOH and Verley acetylation.

From the 60-100-g samples of hydrolyzed copolymer obtained in this way, vulcanizates were prepared*; their mechanical properties are given in Table 6. Before vulcanization the samples were stabilized with 1% N-phenyl-2-naphthylamine. It was noted that the copolymers showed satisfactory technological behavior in the preparation of the vulcanizates.

The data given in Table 6 show that these rubbers have lower glass temperatures than natural rubber (66-71°) [15] and higher stability to gasoline.

SUMMARY

1. Previously undescribed copolymers of butadiene and vinyl formate were prepared. A description was given of the conditions required for the mass copolymerization of these monomers in presence of an oxidation-reduction system consisting of dihydroxymaleic acid, cumene hydroperoxide, and iron naphthenate or stearate.

2. It was shown that the nature of the radical attached to iron affects the rate of copolymerization and the yield of copolymer. It was shown that the use of iron stearate instead of the naphthenate increases the conversion almost fivefold (from 16.2% to 88.2%).

3. Fractionation of the copolymer gave fractions differing in molecular weight but not in chemical composition.

4. It was shown that the formic ester groups of the copolymer can be hydrolyzed, and the effect of free hydroxy groups on certain properties of the polymer was characterized.

5. The copolymerization constants for reaction of butadiene with vinyl formate were determined.

*The vulcanizates were prepared in the Mechanical Testing Laboratory of the All-Union Synthetic Rubber Research Institute.

LITERATURE CITED

[1] S.N. Ushakov, I.A. Arbuzov and E.N. Rostovsky, J. Appl. Chem. 20, 10, 1013 (1947).

[2] W. Kern, Makromol. Chem. 1, 449 (1948).

[3] E. Chilikina and S. Medvedev, J. Phys. Chem. 13, 1201 (1939).

[4] E.I. Tinyakova, B.A. Dolgoplosk and M.B. Rabinovich, Bull. Acad. Sci. USSR, div. chem. sci. 1957, 702.*

[5] F.T. Wall, J. Am. Chem. Soc. 71, 919 (1946).

[6] M.A. Lurye, N.M. Marushkin, et al., Synthetic Rubber 6, 13, 19 (State Chem. Tech. Press, 1934).**

[7] S. Paulstein, Monomers (Foreign Lit. Press, Moscow, 1951), p. 36.***

[8] Yu.S. Zalkind, M. Aizikovich, B. Vovsi and A. Ivanov, Trans. Leningrad Chem. Tech. Inst. 2, 21 (1935).

[9] A.M. Kuhlberg, Organic Syntheses (Goskhimizdat, Moscow-Leningrad, 1947).***

[10] H. Fenton, J. Chem. Soc. (L) 65, 901 (1894).

[11] J.U. Nef, Ann. 357, 291 (1907).

[12] C. Neuberg, Biochem. Z. 71, 112 (1915).

[13] F.R. Mayo and F.M. Lewis, J. Am. Chem. Soc. 66, 1594 (1944).

[14] T. Alfrey, J. Bohrer and H. Mark, Copolymerization (Foreign Lit. Press, Moscow, 1953).***

[15] A.I. Marei, Chemistry and Physical Chemistry of Macromolecular Compounds (Izd. AN SSSR, Moscow, 1952), p. 278.**

Received July 9, 1956

Institute of Macromolecular Compounds
Academy of Sciences, USSR

*Original Russian pagination. See C.B. translation.

**In Russian.

***Russian translation.

OXIDE–METAL CATALYSTS FOR THE REFORMING OF GASOLINES

COMMUNICATION 2. REFORMING OF NARROW GASOLINE FRACTIONS OF ILSK AND SECOND BAKU PETROLEUMS OVER PLATINUM CATALYSTS

Kh.M. Minachev, N.I. Shuikin, N.F. Kononov, I.L. Garanin and M.A. Ryashentseva

In the first communication [1] we gave the results of the reforming of the 96-114° fraction of the straight-run gasoline of Ilsk-Khadyzhin petroleum in a flow system over a $Pt-SiO_2$ catalyst, and these provided the basis for selecting the process schedule (480°, 20 atmos, space velocity v for feed of gasoline 1 $hour^{-1}$, molar ratio of circulating hydrogen to original substance (H_2 : HC) 7-9 : 1). Under these conditions aromatic hydrocarbons were obtained in maximum yield, mainly by dehydrogenation of cyclohexanes, and the undesirable reactions of hydrocracking were reduced to a minimum. However, the stability of the 0.5% $Pt-SiO_2$ catalyst was comparatively low and, after 300 hours in operation, its activity began to fall.

It has recently become particularly important to develop active gasoline-reforming catalysts which are stable and do not require regeneration (in order to obtain aromatic concentrates and high-quality motor and aviation fuels) [2, 3]. Two of the present authors have shown [4, 5] that the catalyst 0.5% $Pt-Al_2O_3$ has high dehydrogenating and isomerizing activity. Thus, in the catalytic treatment of methylcyclohexane in a flow system at 460° and 20 atmos, the substance was dehydrogenated with formation of toluene (82.1%) and isomerization with ring contraction occurred only to a slight extent. Under the same conditions, ethylcyclopentane was isomerized with ring expansion (the yield of toluene was 44%).

In the present investigation we investigated the activity and stability of a 0.5% $Pt-Al_2O_3$ catalyst under the conditions for the reforming of the 95-115° fraction of gasoline from Ilsk petroleums (close in composition to the 96-114° fraction, the transformations of which we investigated previously [1]). Also, in view of the ever-increasing importance of Second Baku petroleums, we studied the transformation of the 85-138° fraction of the gasolines of these petroleums (poorer in naphthenes than the corresponding fractions of Ilsk-Khadyzhin petroleums) over the same catalyst and over the previously [1] investigated 0.5% $Pt-SiO_2$ catalyst with a more severe temperature schedule than that used in the reforming of gasolines of Ilsk petroleums.

EXPERIMENTAL

Preparation of Catalysts

Catalyst No. 1 (0.5% $Pt-Al_2O_3$). Alumina in the form of cylinders, diameter 3 mm and height 5 mm, was roasted and impregnated with a solution of chloroplatinic acid. The catalyst was dried and reduced in a stream of hydrogen. The details of the preparation of the catalyst are given in a previous paper [5]. The specific surface of the catalyst, determined by adsorption of benzene at 0°, was 70 sq·m/g, and that of the original alumina was 90 sq·m/g [5]. About 300 ml of catalyst was loaded into the reactor.

Catalyst No. 2 (0.5% $Pt-SiO_2$). Silica gel (from the Voskresensk Chemical Combine) was first ground down to grains of diameter 1.5-2.5 mm, subjected to special treatment, and roasted. It was then impregnated in a solution of chloroplatinic acid, dried, and reduced in a stream of hydrogen. The details of the preparation are given in the same paper [5]. The specific surface of the catalyst, determined by adsorption of benzene at 0°, was 220 sq·m/g, and that of the original silica gel was 195 sq·m/g [5]. About 300 ml of catalyst was loaded into the reactor.

X-ray analysis of the Catalysts.* The samples were examined under CrK_α radiation (2.285 A) on Agfa Laufilm; exposure 12 hours; 30 kv, 12 ma (vanadium filter). The ground samples were placed in celluloid capillaries, 0.87 mm in diameter. The results were briefly as follows. Catalyst No. 2 (0.5% Pt – SiO_2) gave no lines corresponding to platinum. Catalyst No. 1 (0.5% Pt – Al_2O_3) gave very broad diffuse lines corresponding to the lines of γ-Al_2O_3: the interplanar distances were almost identical with tabulated data for γ-Al_2O_3. However, the reflections from planes with the indices 400 (1.99 A) and 440 (1.39 A) were very close to reflections from the planes 200 and 220: d_{200} for Pt is 1.95 A; d_{220} for Pt is 1.38 A. The lines obtained on the x-ray photographs give us grounds for postulating the presence of crystalline γ-Al_2O_3. We cannot exclude the possibility of the presence of crystalline platinum, for we have shown in previous investigations [6, 7] that, for example, on activated charcoal this metal is in the crystalline state, even when present at the lowest concentrations.

Characterization of the Original Gasoline Fractions

1) The 95-115° fraction of gasolines from Ilsk petroleums had n_D^{20} 1.4116 and d_4^{20} 0.7455; it contained 9.0% by volume of aromatic hydrocarbons and 0.016% by weight of sulfur.

Engler Fractionation

Start of boiling	95.0°	95%	106.5°
10%	101.5°	97.5%	108.5°
50%	103.5°	End of boiling	115°
90%	105°		

The group composition of the fraction was naphthenes 39.0%, paraffins 51.2%, and aromatics 9.8%.

2) The 85-138° fraction of straight-run gasolines of Second Baku had n_D^{20} 1.4506 and d_4^{20} 0.7212; it contained 7.2% by volume of aromatic hydrocarbons and 0.018% by weight of sulfur.

Engler Fractionation

Start of boiling	85°	90%	116°
10%	92.0°	95%	132°
50%	100°	End of boiling	138°

The group composition of the fraction was naphthenes 26.7%, paraffins 65.3%, and aromatics 8.0%.

Apparatus

The reforming experiments were carried out in a block reactor, which was heated electrically and maintained at a temperature constant within ±2°. The measurement and regulation of temperature was carried out with the aid of thermocouples and electronic potentiometers. The catalysis tube (made of stainless steel EYa1T, internal diameter 40 mm, height 800 mm) was fixed in an aluminum block held at temperatures up to 500°. A detailed description of a flow-type apparatus working at pressures of up to 50 atmos with recirculation of gaseous products was described in detail in the first communication [1].

Experimental Procedure

The temperature in the reactor was raised to that required in the experiment while a feeble current of hydrogen was passed; the hydrogen pressure was then raised to the required value. The pump for the feed of gasoline was then started at a predetermined speed, and the circulatory gas pump was switched on (this established the ratio of hydrogen to original hydrocarbons H_2: HC at the required value). The original gasoline was passed over the catalyst for one to two hours (pre-experiment period); in the course of this time the rate of feed of gasoline, the temperature, and the pressure were established at the required values. After removal of the liquid catalysis products that had accumulated in the pre-experiment period, experiments were carried out in which the

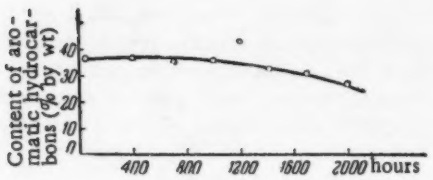
*The x-ray analysis of the catalyzates was carried out by A.M. Rubinshtein, to whom the authors express their thanks.

activity and stability of the catalysts were tested over a long period.

Analysis of Liquid and Gaseous Catalysis Products

For the catalyzates, as in the case of the starting materials, the refractive index, density, and content of aromatics (by the sulfuric acid method) and sulfur compounds were determined, and Engler fractionation was carried out. The gaseous products were analyzed in an Orsat-Lunge apparatus and were found to be mainly hydrogen (up to 98%).

Catalyst No. 1 (0.5% Pt–Al_2O_3) was investigated for stability, activity, and selectivity (mainly its ability to bring about aromatization, rather than hydrogenolysis, isomerization, etc.) in the reforming of the 95-115° fraction of the gasoline of Ilsk petroleums and in the reforming of the 85-138° fraction of gasolines from Second Baku petroleum.



Variation in the content of aromatic hydrocarbons in the catalyzate as a function of the length of service of the catalyst (470-480°; 20 atmos; v = 1 hour^{-1}; $9H_2$:HC).

Catalyst No. 2 (0.5% Pt–SiO_2) was investigated for activity and selectivity in the transformation of the 85-138° fraction of gasolines from Second Baku petroleums.

The results of experiments on the reforming of the 95-115° fraction over Catalyst No. 1 are given in Table 1 and in the graph.

These results show that over a period of 2000 hours Catalyst No. 1 preserved a fairly high activity and selectivity. The content of aromatic hydrocarbons in the catalyzate remained almost unchanged (35-36%) for 1100 hours, and only in the succeeding 900 hours did the concentration fall gradually to 25%. In the course of this time the temperature of the process did not exceed 480° (mean 470°). This catalyst "run" was continued further, and some loss in activity was observed with a slight fall in the content of aromatic hydrocarbons in the catalyzate to 23%. Rise in temperature to 490-500° stabilized the content of aromatic hydrocarbons at 25-26% by weight over a period of almost 800 hours. Owing to the inadequacy of the cooling of the condensation system by running water and the impossibility of using other cooling agents, there were appreciable losses of catalyzate, amounting in some cases to 9%, and this explains why the yield was not as high as it should have been.

TABLE 1

Yields and Compositions of Catalyzates in the Reforming of the 95-115° Fraction of Ilsk Petroleum (470-480°; v = 1 hour^{-1}; 20 atmos; $9H_2$:HC)

No.		Length of run (hours)				
		to 100	100-500	500-1000	1000-1500	1500-2000
1	Yield of liquid catalyzate (on original fraction) (% by weight)	91.0	92.4	90.0	94.0	92.0
2	Start of boiling (°C)	96	96	97	95	97
	End of boiling (°C)	120	124	123	121	121
3	Density of catalyzate d_4^{20}	0.7678	0.7674	0.7680	0.7674	0.7664
4	Yield of gas (on original material) (% by weight)	0.7	0.7	0.7	1.6	0.9
5	Losses (% by weight)	8.2	6.9	9.3	8.0	7.1
6	Composition of catalyzate (% by weight)					
	a) aromatic hydrocarbons	36.0	36.0	35.0	32.0	25.4
	b) naphthenes and paraffins	64.0	64.0	65.0	68.0	74.6
7	Composition of recycled gas (% by volume)					
	a) hydrogen	98	98	98	98	98
	b) C_1–C_4 saturated hydrocarbons	2	2	2	2	2
8	Sulfur content of catalyzate (% by weight)	0.006	0.005	0.007	0.006	0.007

In the reforming of the fraction only very slight gas formation was observed. The yield of gas did not exceed 1.6% on the amount of starting material, and the circulating gas mixture contained up to 98% of hydrogen. This fact indicates the highly selective properties of the catalyst. Apart from the loss of gasoline resulting from appreciable gas formation (as in hydroforming [8], in which it attains 15% and more), the presence of hydrocarbons in the recycling gases lowers the partial pressure of hydrogen and so worsens the conditions for the working of the catalyst (it leads to increased coke formation [9]). As analysis of spent Catalyst No. 1 showed, its carbon content was only 0.46%, which indicates only very slight coke formation. It should be noted also that sulfur compounds, originally present in an amount of 0.016% (calculated as sulfur), do not deactivate our catalyst. The sulfur content of the catalyzate fell on the average to 0.006% (i.e., to almost one-third of that of the original fraction). Hence, Catalyst No. 1 effected also some desulfurization of the 95-115° fraction.

In the process of work over one volume of catalyst, 2460 volumes of gasoline was passed, i.e., 1 g of Pt effected the reforming of 755 liters of the original fraction.* Judging from the fractionation results, the fractional compositions of the catalyzates over the whole period of service of the catalyst differed very little indeed from the fractional composition of the original material, which again indicates the insignificant amount of low-boiling paraffins in the catalyzate and therefore the small contribution of hydrocracking reactions under the given conditions.

TABLE 2

Yields and Compositions of Catalyzates in the Reforming of the 85-138° Fraction of Second Baku Gasolines (495-500°; v = 1 hour^{-1}; 20 atmos; $9H_2$:HC)

	Catalyst No. 1 (0.5% Pt–Al_2O_3)	Catalyst No. 2 (0.5% Pt–SiO_2)
Yield of catalyzate (on original fraction) (% by weight)	95	90.0
Start of boiling (°C)	59	53
End of boiling (°C)	140	152
Density of catalyzate d_4^{20}	0.7400	0.7321
Composition of catalyzate (% by weight)		
a) aromatic hydrocarbons including:	29.2	23.1
benzene	3.2	5.4
toluene	15.2	12.6
xylenes + ethylbenzene	10.8	5.1
b) naphthenes and paraffins	70.8	76.9
Composition of recycled gas (% by volume)		
a) hydrogen	96.5	90.6
b) C_1–C_4 saturated hydrocarbons	3.5	9.4

The reforming of the 85-138° fraction of Second Baku gasolines over Catalysts No. 1 and 2 was carried out under the following conditions: 495-500°; 20 atmos; v = 1 hour^{-1}; $9H_2$:HC. Catalyst samples (about 300 ml each) were placed in the block catalysis tube and the experiments were carried out as described above. The data on yields and compositions of catalyzates and gaseous products (after 100 hours of continuous work of catalysts) are given in Table 2.

According to Table 2, maximum yield of catalyzate of high aromatic content was obtained by passage of the 85-138° fraction over Catalyst No. 1 (0.5% Pt–Al_2O_3). Gas formation was then much less than in the case of Catalyst No. 2 (0.5% Pt–SiO_2), which is confirmed by the analysis of recycled gas. It is clear that the lowering of yield of catalyzate from 95% to 90% when Catalyst No. 2 is used instead of No. 1 is to be attributed to increased gas formation. The increased hydrocracking of hydrocarbons over Catalyst No. 2 can be explained by the much higher (almost threefold) specific surface of this catalyst, as compared with that of Catalyst No. 1. The

*The amount of 0.5% Pt catalyst was 320 ml (212 g, the bulk density being 0.67); the amount of Pt was 1.07 g, and the amount of gasoline passed was 808 liters.

probability of this view is confirmed by the fact that, in the investigations of Chapett and others [10], reduction in the hydrocracking activity of nickel on aluminum silicate was attained by suitable reduction of the specific surface of the catalyst.

SUMMARY

1. A study was made of the activity and stability of a 0.5% Pt–Al_2O_3 catalyst under the conditions of reforming of the 95-115° fraction of the gasoline from Ilsk petroleums. It was shown that, under the conditions selected for the process, the catalyst preserved its stability and maintained a fairly high activity over a period of 2000 hours.

2. A comparative study was made of the catalytic properties of two platinum catalysts under the conditions of reforming of the 85-138° fraction of Second Baku gasolines. It was shown that the catalyst 0.5% Pt–Al_2O_3 has considerable advantages (higher yield of aromatic hydrocarbons with less gas formation) over the catalyst 0.5% Pt – SiO_2.

3. It was shown that the catalyst 0.5% Pt–Al_2O_3 may be used for the reforming of narrow gasoline fractions with the object of obtaining aromatic hydrocarbons. The catalyst has only feeble hydrocracking properties and so is superior to catalysts used in the hydroforming process for the present purpose.

LITERATURE CITED

[1] Kh.M. Minachev, N.I. Shuikin, M.A. Ryashentseva and N.F. Kononov, Bull. Acad. Sci. USSR, div. chem. sci. 1957, 1223.*

[2] J.G. Echouse, Petrol. Eng. 26, No. 4, C-26 (1954).

[3] J.C. Dart, A.G. Oblad and H.Heinemann, Erdöl u. Kohle N1, 9 (1955).

[4] Kh.M. Minachev, N.I. Shuikin, E.D. Tulupova and Yu.P. Egorov, Proc. Acad. Sci. USSR 99, 777 (1954).

[5] N.I. Shuikin, Kh.M. Minachev, L.M. Feofanova, E.G. Treshchova, T.P. Yudkina and A.E. Agronomov, Bull. Acad. Sci. USSR, div. chem. sci. 1955, 501.*

[6] A.M. Rubinshtein, Kh.M. Minachev and N.I. Shuikin, Proc. Acad. Sci. USSR 62, 497 (1948).

[7] A.M. Rubinshtein, Kh.M. Minachev and N.I. Shuikin, Proc. Acad. Sci. USSR 67, 287 (1949).

[8] C.W. Tyson, Fourth World Petrol. Congress, Proceedings, Sect. III/D (Rome, 1955).

[9] V.I. Karzhev, D.I. Orochko and E.M. Kheifen, Trans. All-Union Gas and Synthetic Liquid Fuel Research Inst. No. 2 (Moscow-Leningrad, 1950), p. 104.**

[10] F. Morton, Chem. Age 68, 71 (1953).

Received June 29, 1956

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

*Original Russian pagination. See C.B. translation.

**In Russian.

SYNTHESIS OF POLYALKYLENEARYLS*

COMMUNICATION 1. POLYCONDENSATION OF METHYLENE CHLORIDE WITH HALOBENZENES

G.S. Kolesnikov, V.V. Korshak and T.V. Smirnova

We recently described results on the polycondensation of methylene chloride with benzene in presence of aluminum chloride and showed that in this case the reaction takes a different course than in the polycondensation of 1,2-dichloroethane with benzene. In other investigations we determined the effect of the presence of substituents in aromatic hydrocarbons on the course of the polycondensation of these hydrocarbons with 1,2-dichloroethane [2-5]. The present investigation had the object of determining the effect of the presence of a substituent in the aromatic hydrocarbon on the course of its polycondensation with methylene chloride. As substituted aromatic hydrocarbons we selected fluoro-, chloro-, and bromobenzenes. The procedure was the same as in the case of the polycondensation of methylene chloride with benzene [1]. The reactants were taken in equimolecular proportions; the concentration of aluminum chloride was nine moles percent on the amount of substituted aromatic hydrocarbon. The results are given in Table 1.

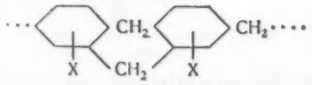
TABLE 1

Polycondensation of Methylene Chloride with Halobenzene

Halobenzene	Low-mol. wt. polycondensation product and its yield (%)	Macromolecular polycondensation product and its yield (%)	Molecular wt. of polycondensation product
Fluorobenzene	Bisfluorophenylmethane, 19.6	Poly[methylene(fluorophenyl)], 40.7	1940
Chlorobenzene	Bischloromethylmethane, 12.0	Poly[methylene(chlorophenyl)], 52.5	1920
Bromobenzene	p-Dibromobenzene,* 11.0	Poly[methylene(bromophenyl)], 38.4	2510

*By-product, formed in side reaction.

In no case was the formation of insoluble three-dimensional products observed. It may be supposed that this arises either from the low activity of halobenzenes or from the formation of dihydroanthracene ring systems in the growing chain of poly[methylene(halophenyl)]. The molecular weights of the polymers obtained were low, which may be explained by chain termination as a result of the formation of dihydroanthracene ring systems at the ends. Analysis of fractions obtained by treatment of the polymers with hot alcohol shows that formation of dihydroanthracene ring systems probably does occur, for the analysis of alcohol-insoluble fractions agrees closely with values calculated for the structural units



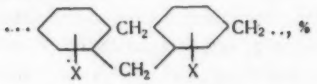
*The preceding communication in this series was published in the series "Macromolecular Compounds."

in which X is a halogen atom, the position of which is unknown.

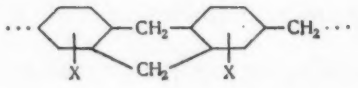
The analytical results for the polymers and the calculated contents of the elements are given in Table 2.

TABLE 2

Characteristics of Products of the Polycondensation of Methylene Chloride with Halobenzenes

		Halobenzene	
		fluorobenzene	chlorobenzene
Alcohol-soluble fraction			
Found (%):		77.60	67.25
		77.46	67.52
	H	4.72	4.20
		4.43	4.24
	X	17.22	27.84
		17.35	27.75
Molecular weight		820	1050
Calculated for			
$-C_6H_3XCH_2-$, (%) :	C	77.77	67.48
	H	4.66	4.04
	X	17.57	28.48
Alcohol-insoluble fraction			
Found (%):		80.36	69.59
		80.26	69.80
	H	4.33	4.00
		4.38	4.03
	X	14.54	26.18
		14.67	26.40
Molecular weight		1790	3450
Calculated for			
			
	C	78.94	68.73
	H	4.42	3.84
	X	17.04	27.43

It will be seen from Table 2 that the alcohol-soluble and alcohol-insoluble fractions differ in composition, the carbon content of the latter being greater than that of the alcohol-soluble fraction. This can be explained by the presence of dihydroanthracene ring systems in the chain of alcohol-insoluble polymers. Alcohol-insoluble fractions probably consist in the main of



units, and alcohol-soluble fractions of $-C_6H_3XCH_2-$ units (X is halogen).

The polycondensation of methylene chloride with halobenzenes gives not only macromolecular products, but also products of low molecular weight formed in the initial stage of polycondensation. In the polycondensation of methylene chloride with fluorobenzene we isolated a liquid of b.p. 103-104° (4 mm), indicated by elementary analysis to be bisfluorophenylmethane.

Found %: C 76.87, 76.69; H 5.28, 5.07. $C_{13}H_{10}F_2$. Calculated %: C 76.45; H 4.94.

We did not succeed in establishing the structure of the bisfluorophenylmethane.

In the polycondensation of methylene chloride with chlorobenzene we isolated bischlorophenylmethane as a liquid of b.p. 139-142° (4 mm). The chlorine content was in close agreement with the calculated value:

Found %: Cl 30.10, 29.80. $C_{13}H_{10}Cl_2$. Calculated %: Cl 29.91.

The bischlorophenylmethane was oxidized with chromium trioxide: a product was obtained having a chlorine content approximating to that of dichlorobenzophenone:

Found %: Cl 27.58, 27.76. $C_{13}H_8OCl_2$. Calculated %: Cl 28.24.

However, the melting point of the oxidation product, 100-101.5°, was not identical with that of any one of the known dichlorobenzophenone isomers. Thus, the following melting points have been reported [6]:

Isomer	M.p. (°C)
o, o'-	45-46
m,m'-	123.8-124.9
m, o'-	Oil
o, p'-	62-65
m, p'-	112.6-113.4
p, p'-	146

The product that we obtained by oxidizing bischlorophenylmethane was apparently a mixture of two or more bischlorophenylmethane isomers, difficult to separate by crystallization.

In the polycondensation of methylene chloride with bromobenzene the main low-molecular-weight product obtained was p-dibromobenzene. The formation of this is to be explained by the transfer of a bromine atom from one bromobenzene molecule to another under the influence of aluminum chloride. As early as 1882 Dumreicher [7] observed the formation of dibromobenzene and benzene when bromobenzene was heated with aluminum chloride. In the polycondensation of methylene chloride with bromobenzene in presence of aluminum chloride partial conversion of bromobenzene into dibromobenzene occurred and we were able to isolate it. This reaction probably occurs mainly at the start of the polycondensation process when the concentration of bromobenzene is high; but the possibility of the formation of dibromobenzene at later stages cannot be excluded. Similar transfer of halogen occurs also in the polycondensation of 1,2-dichloroethane with o-dichlorobenzene [4]. p-Dibromobenzene was identified from its melting point, its mixture melting point, its molecular weight, and its bromine content.

Found %: Br 66.58, 66.60; M 233.0, 229.2. $C_6H_4Br_2$. Calculated %: Br 67.76; M 235.93.

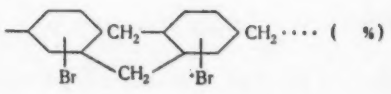
Apart from p-dibromobenzene, bisbromophenylmethane was formed as a low-molecular-weight reaction product. Oxidation gave dibromobenzophenone, m.p. 125-128°.

Found %: Br 46.75, 47.30. $C_{13}H_8OBr_2$. Calculated %: Br 47.01.

According to the literature, the isomer of closest melting point (130°) is 3,4'-dibromobenzophenone [8].

The transfer of bromine atoms from some aromatic molecules to others explains the low bromine content of the macromolecular polycondensation products.

The polymer fraction that was soluble in hot alcohol had the composition (%): C 50.59, 50.87; H 3.49, 3.37; Br 45.60, 45.42. The insoluble fraction contained (%): C 59.62, 59.70; H 3.20, 3.45; Br 36.60, 36.82. The calculated composition of the structural unit $C_6H_3BrCH_2$ (%) is C 49.74; H 2.98; Br 47.28; and for the unit



C 51.46; H 2.88; Br 45.66.

The investigation shows that monohalobenzenes polycondense with methylene chloride in presence of aluminum chloride. In these cases the polycondensation proceeds as in the polycondensation of methylene chloride with benzene, but reaction with bromobenzene is complicated by side reactions in which halogen moves from some aromatic molecules to others. The presence of the halogen atom has no substantial effect on the course of the polycondensation process: the molecular weights and yields of the products differ little from those found for the polycondensation of methylene chloride with benzene [1]. There is some change in the character of the resins obtained: instead of the brittle solid obtained by the polycondensation of methylene chloride with benzene, in the polycondensation of methylene chloride with halobenzenes, viscous liquids are obtained.

SUMMARY

The polycondensation of methylene chloride with fluoro-, chloro-, and bromobenzenes was studied.

LITERATURE CITED

[1] G.S. Kolesnikov, V.V. Korshak and T.V. Smirnova, Bull. Acad. Sci. USSR, div. chem. sci. 1957, 375.*

[2] G.S. Kolesnikov, V.V. Korshak and L.S. Fedorova, Bull. Acad. Sci. USSR, div. chem. sci. 1955, 859.*

[3] G.S. Kolesnikov, V.V. Korshak and T.A. Soboleva, Bull. Acad. Sci. USSR, div. chem. sci. 1955, 1095.*

[4] G.S. Kolesnikov and V.V. Korshak, Bull. Acad. Sci. USSR, div. chem. sci. 1955, 1100.*

[5] G.S. Kolesnikov, V.V. Korshak, M.A. Andreeva and A.I. Kitaigorodsky, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 114.*

[6] H.L. Haller et al., J. Am. Chem. Soc. 67, 1591 (1945).

[7] O. Dumreicher, Ber. 15, 1886 (1882).

[8] F. Kunskell, Ber. 37, 3484 (1904).

Received June 30, 1956

Institute of Heteroorganic Compounds
Academy of Sciences, USSR

*Original Russian pagination. See C.B. translation.

BRIEF COMMUNICATIONS

EFFECT OF FINE VIBRATIONAL MILLING ON THE ACTIVITY OF RANEY NICKEL

S.L. Kiperman, A.A. Balandin and I.R. Davydova

Raney catalysts, prepared by leaching the appropriate alloys, now find extensive application, particularly in liquid-phase reactions. However, adequate attention is not generally paid to such an important factor in determining the activity of a catalyst as the dispersity; all the more so since these catalysts are generally used in powder form. In order to determine the effect of the dispersity of a catalyst on its activity, we applied the method of fine vibrational milling to nickel-aluminum alloys.

EXPERIMENTAL

The alloy, which contained 50% of nickel, was ground in a vibromill.* It was leached with double the theoretical amount of 25% NaOH ("Chemically Pure") in the cold, and was then heated for two hours at 100° and washed in a stream of pure hydrogen.

The dimensions of the particles were determined, before and after leaching, by sedimentation analysis with the aid of a sensitive tungsten spiral, the extension of which was determined with a cathetometer. Water and glycerol were used as dispersion means. The specific surfaces of the catalysts were determined by the adsorption of palmitic acid from alcoholic solutions [1], which gave values in accord with those obtained by the Brunauer-Emmett-Teller method.

TABLE

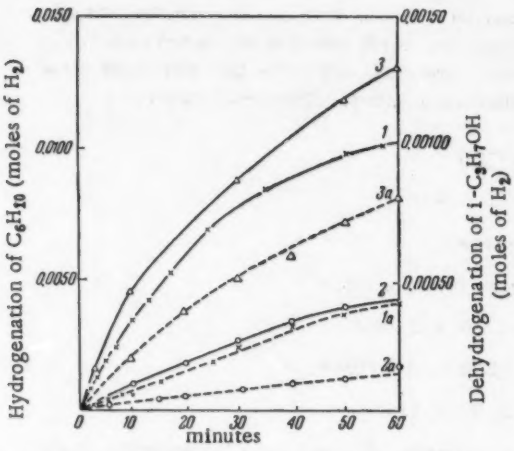
Grinding	Predominant radius of particles (μ)		Specific surface (sq·m/g)	Specific activity $k \cdot 10^{11}$ molecules/sq·cm·sec	
	before leaching	after leaching		for hydrogenation of C_6H_{10}	for dehydrogenation of $i\text{-}C_3H_7OH$
Ordinary	100-150	70-125	34	1.53	3.92
In vibromill	3	3	48	6.24	6.22

As will be seen from the table, samples subjected to vibrational milling differ greatly from the original samples, their particles being of the same order of size as the minimum dimensions of the coarse pores; leaching has very little effect on the dimensions of the fine particles.

For the characterization of the activity of the catalyst we selected the reactions of hydrogenation of cyclohexane in ethanol and dehydrogenation of isopropyl alcohol. Starting materials: cyclohexene, b.p. 83° (762 mm), n_D^{21} 1.4451; absolute ethanol, b.p. 77.5-78.0° (750 mm); n_D^{20} 1.3618; absolute isopropyl alcohol, b.p. 81.0-81.5° (754 mm); n_D^{20} 1.3780. The reactions were studied in a thermostated vessel having two condensers (fused together in one piece) and clamped in a shaker. The course of the reaction was judged by the amount of hydrogen absorbed or evolved. The hydrogenation of cyclohexene was studied in 2.5% and 5% solutions in ethanol with 0.25 g and 0.5 g of catalyst (freshly prepared and also after long keeping) at 25° with shaking at a frequency of 400-800

*The vibration mill was constructed in the All-Union Structural Materials Research Institute under the supervision of R.L. Kayushina, to whom we express our sincere thanks.

per minute, which ensured the absence of diffusional retardation. The dehydrogenation of isopropyl alcohol was studied at the boiling point of the alcohol in the same apparatus with shaking at a frequency of 700-800 per minute, at which the effect of diffusional retardation was small. Before the start of reaction the catalyst was saturated with pure hydrogen for a long time. The exact dosage of catalyst was ensured by the procedure developed previously [2]. As will be seen from the graph, the activities of catalysts subjected to vibrational milling are considerably higher than those of catalysts ground in the usual way.



Effect of vibrational milling on catalyst activity: _____ ordinarily ground catalyst; _____ finely ground catalyst; 1) and 1a) hydrogenation of C_6H_{10}; 2) and 2a) hydrogenation of C_6H_{10} after catalyst had been kept for a long time; 3) and 3a) dehydrogenation of 1-C_3H_7OH.

Liquid-phase reaction with adequate agitation can be regarded as analogous to gas-phase reaction in a static system. Hence, from the curves expressing the relation of the amount x of product formed to the time t we may find reaction rates dx/dt from the slopes of the curve at various points. The analysis of curves plotted on a large scale shows that at the start of reaction, hydrogenation is of zero order with respect to cyclohexene at constant hydrogen concentration (owing to continuous replacement of loss from solution). Beyond the initial section there is a retardation of reaction, greater or smaller according to the activity of the catalyst, this being probably conditioned by the extent of simultaneous "irreversible catalysis" [3] proceeding at the surface with formation of benzene, which is hydrogenated slowly and renders an ever-increasing proportion of the surface ineffective. Special experiments showed that there was no benzene in the liquid phase, but a preliminary washing of the catalyst with benzene reduced its activity. The poisoning effect of benzene on a nickel catalyst has been observed in several investigations [4-6]. The activity of a catalyst can therefore be characterized by the values of constants calculated for initial rates of zero order. In the case of dehydrogenation, zero-order reaction was again observed at the start, and there was subsequent retardation; this will be examined in a separate paper. The table shows the relation of the rate constants of the two reactions, expressed in terms of unit surface of catalyst, to the extent of grinding.

To explain the effect of vibrational milling on catalyst activity further investigations are required. At present we may make the following observations: 1) increase in activity may arise from change in the microroughness of the surface due to the appearance of dislocations during the mechanical treatment of the metal; owing to rapid lateral diffusion, places in the deep pores may become accessible; 2) on the other hand, in samples ground in the usual way part of the internal pores may be inaccessible for reaction. Fine grinding results in the opening up of the internal surface. Since we attained a dispersity that approximated to that of the larger pores, we may consider, very roughly, that in this way we achieved complete accessibility of the internal surface for ordinary diffusion. We may then calculate the degree of utilization f of the catalyst surface with the aid of equations that follow from Wheeler's work [7] and a comparison of initial reaction rates on the ordinary and finely ground catalysts: $f = \frac{1}{2n/2h}$, in which n is the reaction order, h is a dimensionless parameter depending on the effective diffusion coefficient D in the pores, the diameter a of the grains, the mean radius r of the pores, and the "true" rate constant k, characterizing the activity of unit surface of a "nonporous" catalyst at unit concentration (the concentration C at the mouths of the pores being regarded as the same as the bulk value), $h \approx \approx \frac{a}{3}\sqrt{\frac{kC^{n-1}}{rD}}$. From this we may evaluate approximately the diffusion coefficient for C_6H_{10} in the pores of the catalyst, assuming provisionally that $r \approx 1\mu$. Substituting appropriate values, we obtain $D = 6.7 \cdot 10^{-6}$ sq·cm/sec. According to another criterion from the same source [7], for a static system $hth \cdot h = \frac{0.693\, a^2 V_R}{18 D t_{1/2} V_g W}$, in which $t_{1/2}$ is the time for half-conversion, W is the weight of catalyst, V_R is the total volume, V_g is the volume of pores.

Substituting $t_{1/2} = 4200$ seconds, $W = 0.25$ g, $V_R = 40$ cc, $V_g = 0.06$ cc/g, and $h \approx 4$, we obtain $D \approx 1.0 \cdot 10^{-5}$ sq·cm/second. When we take account of the order of diffusion coefficients in the liquid phase (10^{-5}-10^{-6} sq·cm/second) and the approximate nature of the calculation, we may regard the results of the calculation as close to actuality.

Laboratory worker G.I. Brusova took part in the work.

SUMMARY

The activities and specific activities of Raney nickel catalysts that have been first subjected to fine grinding in a vibrational mill for the hydrogenation of cyclohexene and the dehydrogenation of isopropyl alcohol in the liquid phase are higher than the activities of catalysts ground in the usual way. This fact is probably associated with change in the microroughness of the surface or the presence of internal diffusional retardation.

LITERATURE CITED

[1] H.C. Smith and J.F. Fuzek, J. Am. Chem. Soc. 68, 229 (1946).

[2] S.L. Kiperman and I.R. Davydov, Works Lab. (in the press).

[3] N.D. Zelinsky, Selected Works (Izd. AN SSSR, Moscow, 1941), p. 195.*

[4] A.A. Alchudzhan and A.A. Vvedensky, J. Gen. Chem. 16, 415 (1946).

[5] A.A. Balandin and S.L. Kiperman, Proc. Acad. Sci. USSR 63, 387 (1948).

[6] B.D. Polkovnikov, Thesis, Div. Chem. Sci. Acad. Sci. USSR, 1957.

[7] E. Wheeler, in the collection: "Catalysis; Theory and Methods of Investigation" (Foreign Lit. Press, Moscow, 1955), p. 479.**

Received July 9, 1957

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

*In Russian.

**Russian translation.

1-NAPHTHYL COMPOUNDS OF THE TYPE $ArPbX_3$

V.I. Lodochnikova, E.M. Panov and K.A. Kocheshkov

Organolead compounds containing the 1-naphthyl group have received little study. Several compounds of a mixed type have been described, e.g., $(C_6H_5)_3Pb(\alpha\text{-}C_{10}H_7)$ [1], $(C_6H_5)_2Pb(\alpha\text{-}C_{10}H_7)_2$ [2], $(C_2H_5)_3Pb(\alpha\text{-}C_{10}H_7)$ [3] and also tri-1-naphthyllead [4] obtained in 6-10% yield by the action of 1-naphthylmagnesium bromide (or 1-naphthyllithium) on lead chloride.

As we had two methods, based on our investigations [5, 6], at our disposal for the preparation of organolead compounds of the type $ArPbX_3$, we made use of one of these to prepare some previously inaccessible 1-naphthyl compounds of this type:

$$(\alpha\text{-}C_{10}H_7)_2Hg + Pb(OOCR)_4 \rightarrow \alpha\text{-}C_{10}H_7Pb(OOCR)_3 + \alpha\text{-}C_{10}H_7HgOOCR,$$

in which OOCR is an acetic or isobutyric residue.

By the action of ammonia on the triacetate we obtained 1-naphthaleneplumbonic acid, and by transacylation the triacetate was converted into the tribenzoate. 1-Naphthyl compounds of the type $ArPbX_3$ are slightly yellowish substances, soluble in organic solvents (1-naphthaleneplumbonic acid is insoluble), and insoluble in water (hydrolysis).

EXPERIMENTAL

1-Naphthyllead triacetate. In small portions, 5 g (1 molecular proportion) of di-1-naphthylmercury was added to a solution of 4.9 g (1 molecular proportion + 15% excess) of lead tetraacetate in 50 ml of dry chloroform acidified with a few drops of acetic acid. The mixture became brownish-red; after 90 minutes, reaction was complete. The mixture was cooled to 0° and a solution of 1 equivalent of hydrogen chloride in 4.9 ml of alcohol was added dropwise. The precipitate was filtered off; it amounted to 3.5 g (87%) and consisted of 1-naphthylmercury chloride, m.p. 191° (the literature [7] gives 191°). The filtrate was placed in a vacuum desiccator until solvent had been removed. The brown residue was crystallized from ethyl acetate with the addition of one or two drops of acetic acid. The product, amounting to 3.1 g (55.1%), was a yellowish substance, m.p. 168-169°, unchanged by recrystallization.

Found %: Pb 40.66, 40.14. $C_{16}H_{16}O_6Pb$. Calculated %: Pb 40.52.

Determination of the number of acid groups gave 3.1.

1-Naphthyllead triacetate forms slightly yellowish plates (from ethyl acetate), readily soluble in methanol, ethanol, chloroform, benzene, xylene, and glacial acetic acid.

1-Naphthyllead triisobutyrate. In small portions 1 g (1 molecular proportion) of di-1-naphthylmercury was added to a solution of 1.26 g (1 molecular proportion + 15% excess) of lead tetraisobutyrate in 15 ml of chloroform acidified with some drops of isobutyric acid. One portion was not added until the previous one had dissolved. The operation required 40-45 minutes. The organomercury compound was separated in the usual way. The solution was left in the air until the solvent had evaporated completely. The residue solidified completely (about 1.2 g, m.p. 95-97°). Recrystallization from a hexane-isopentane mixture raised the melting point to 99.5-101°, unchanged by further recrystallization; yield 0.6 g (46%).

1-Naphthyllead triisobutyrate is a faintly yellowish crystalline substance, readily soluble in ethyl acetate, moderately soluble cold and very soluble hot in chloroform, ether, and organic acids (acetic and propionic).

Found %: Pb 35.27, 35.31. $C_{22}H_{28}O_6Pb$. Calculated %: Pb 34.78.

Determination of the number of acid groups gave 2.96.

1-Naphthaleneplumbonic acid. A solution of 2.5 g of 1-naphthyllead triacetate in 60 ml of methanol was poured with mechanical stirring into 75 ml of 5% aqueous ammonia. Reaction proceeded with slight evolution of heat. The mixture was stirred for two hours and then left overnight. The precipitate was filtered off at the pump, washed with water and once with ether, and vacuum-dried for one hour at 100°; yield 1.12 g (62.6%).

Found %: Pb 56.09, 56.32. $C_{10}H_8O_2Pb$. Calculated %: Pb 56.42.

1-Naphthaleneplumbonic acid is a yellow amorphous substance. When placed in a bunsen flame it burns with a flash. The inadequately dried substance bursts into flame when mixed with concentrated sulfuric acid. It is almost insoluble in 50% potassium hydroxide and in concentrated hydrochloric acid*; when treated with glacial acetic acid it is converted into 1-naphthyllead triacetate (see above).

Preparation of 1-naphthyllead triisobutyrate from 1-naphthaleneplumbonic acid. 1-Naphthaleneplumbonic acid (0.32 g, i.e., 1 molecular proportion) and 0.47 g (6 molecular proportions) of isobutyric acid were carefully ground together. The reaction mixture was left in a desiccator over solid caustic alkali. The crystalline substance (0.21 g) that separated on the next day melted at 97-99.5°, raised by crystallization from hexane to 99.5-101°, which corresponds to the melting point of 1-naphthyllead triisobutyrate prepared by the direct method (see above).

1-Naphthyllead tribenzoate. Benzoic acid (0.23 g, i.e., 3 molecular proportions) was added to a hot solution of 0.32 g (1 molecular proportion) of 1-naphthyllead triacetate in a mixture of 5 ml of dry benzene and 2.5 ml of hexane; the acid dissolved rapidly. On the next day the mixture was placed in a refrigerator until crystallization was complete. The precipitate was filtered off, washed with 3-4 ml of dry benzene, and dried in a desiccator over paraffin. The product, amounting to 0.17 g (40.5%), had m.p. 173-174°, unchanged by recrystallization from hexane.

Found %: Pb 29.86, 29.60. $C_{31}H_{22}O_6Pb$. Calculated %: Pb 29.71.

1-Naphthyllead tribenzoate is a light-yellow crystalline substance, extremely soluble in chloroform and very soluble in ethyl acetate and benzene; in methanol it is sparingly soluble cold but readily soluble hot; in hexane and petroleum ether it is sparingly soluble cold and moderately soluble hot. It is insoluble in ether, even hot.

SUMMARY

For the first time 1-naphthyl compounds of the type $ArPbX_3$ have been prepared: 1-naphthyllead triacetate, triisobutyrate, and tribenzoate; also 1-naphthaleneplumbonic acid. The properties of these compounds were studied.

LITERATURE CITED

[1] H. Gilman, E. Towne and K. Jones, J. Am. Chem. Soc. 55, 4689 (1933).

[2] E. Krause and M. Schmitz, Ber. 52, 2150 (1919).

[3] G. Grüttner and Gert.Grüttner, Ber. 51, 1293 (1918).

[4] H. Gilman and H. Bailie, J. Am. Chem. Soc. 61, 731 (1939).

[5] E.M. Panov and K.A. Kocheshkov, Proc.Acad. Sci. USSR 85, 1037 (1952).

*It is probably decomposed to lead dichloride.

[6] E.M. Panov, V.I. Lodochnikova and K.A. Kocheshkov, Proc. Acad. Sci. USSR 111, 1042 (1956).*

[7] A.N. Nesmeyanov, J. Russ. Chem. Soc. 61, 1393 (1929).

Received July 5, 1957

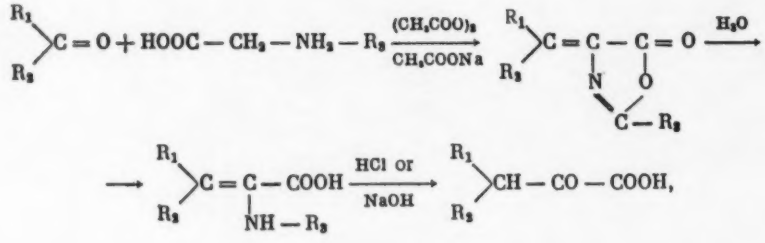
L.Ya. Karpov Physicochemical Institute
and
Sverdlovsk State Medical Institute

*Original Russian pagination. See C.B. translation.

SYNTHESIS OF α-KETO ACIDS VIA AZLACTONES OF 2-(ACYLAMINO)-3-ALKYL(OR ARYL)ACRYLIC ACIDS, AND A NEW SYNTHESIS OF 3-METHYL-2-OXOVALERIC ACID

Z.S. Kagan

Various general methods have been proposed for the synthesis of α-keto acids [1], but although some α-keto acids, in particular aromatic acids, are generally prepared by the condensation of aldehydes with N-acylglycines with formation of azlactones of 2-(acylamino)-3-arylacrylic acids, which are subsequently hydrolyzed, this method of synthesis is nevertheless not regarded as general. This reaction, however, is, in fact, general and proceeds as follows:



in which R_1 is aryl or alkyl, R_2 is alkyl or H, and R_3 is acyl (benzoyl or acetyl).

The synthesis of azlactones of α-benzamidocinnamic acids by the condensation of aromatic aldehydes with hippuric acid was first proposed by Plochl [2]. Condensation of veratraldehyde in this way is now used for the preparation of the azlactone of α-benzamido-3,4-dimethoxycinnamic acid [3], which gives (3,4-dimethoxyphenyl)pyruvic acid by alkaline hydrolysis [4]. By the condensation of 3-indolecarboxaldehyde, an azlactone is formed which is hydrolyzed by alkali to 3-indolepyruvic acid [5, 6]. Phenylpyruvic acid is synthesized similarly, but N-acetylglycine is used instead of hippuric acid; hydrolysis of the azlactone gives α-acetamidocinnamic acid [7], which can be split with alkali [8] or acid [9]. The azlactone of α-benzamidocinnamic acid has been prepared also by the action of benzoic anhydride on phenylserine [10].

Azlactones of aliphatic derivatives of acrylic acid have been used to a considerably less extent in the synthesis of α-keto acids. Thus, 3-methyl-2-oxobutyric acid was prepared by hydrolysis of the azlactone synthesized by condensation of acetone with hippuric acid [11, 12]. The same azlactone was obtained by the condensation of 3-hydroxyvaline with benzoic anhydride [13]. The azlactone of 2-benzamidocrotonic acid was prepared by the condensation of DL-threonine or DL-allothreonine with benzoyl chloride in pyridine [14], of acetaldehyde with hippuric acid [14], or of threonine with benzoic anhydride [13]. Hydrolysis of this azlactone gave 2-oxobutyric acid [14]. Hence, the hydrolysis of azlactones appears to be yet another general method for the synthesis of α-keto acids.

In the course of a study of the biosynthesis of valine and isoleucine in green plants carried out by us in V.L. Kretovich's laboratory, the need arose for the synthesis of keto analogs of these amino acids. We verified the synthesis of 3-methyl-2-oxobutyric acid by the method indicated [11, 12] and attempted the synthesis of 3-methyl-2-oxovaleric acid.

EXPERIMENTAL

Synthesis of 3-methyl-2-oxobutyric acid. A mixture of 100 g of hippuric acid, 250 g of acetone, 100 g of sodium acetate, and 190 g of acetic anhydride (all reactants were first purified and dried) was heated in a water bath for six hours. The orange liquid was cooled and poured into a large amount of water. The orange precipitate of azlactone was washed with water, with dilute sodium carbonate solution, and again with water. Crystallization from boiling aqueous alcohol gave almost colorless needles, m.p. 98-99° (the literature gives m.p. 98-99° [11], 99-100° [12], and 100.2-101.2° [13]). Some more azlactone was extracted from the alcoholic mother liquor by dilution with water and filtration; yield 34.5 g. The azlactone (32 g) was hydrolyzed with 180 ml of concentrated hydrochloric acid in a water bath for six hours. The mixture was cooled, the precipitate was filtered off, and the orange filtrate was repeatedly extracted with ether. The slightly yellowish ethereal solution was dried over sodium sulfate, and the residue after removal of ether was vacuum-distilled. 3-Methyl-2-oxobutyric acid had b.p. 55° (3 mm) and 65° (11 mm) (the literature gives b.p. 65° (11 mm), 65-69° (10 mm) [15], 65-67° (10 mm) [16], 170-175° at ordinary pressure [17]). The white plate-like crystals of this acid had m.p. 16.5° (the literature gives m.p. 16° [11], 31° [16]). The yield was 6.3 g. In order to obtain the sodium salt the crystals were dissolved in a little water and the solution was neutralized with dry sodium bicarbonate and brought to dryness in a vacuum desiccator. Precipitation of the sodium salt with cold acetone, as proposed for the preparation of sodium pyruvate [18], results in considerable losses. The 2,4-dinitrophenylhydrazone had m.p. 194° (the literature gives 194° [12] and 194-195° [19]).

Synthesis of 3-methyl-2-oxovaleric acid. The procedure was as described for 3-methyl-2-oxobutyric acid, but acetone was replaced by 2-butanone (310 g). However, when the orange reaction mixture was poured into a large amount of water, no precipitate formed, but a heavy oily orange liquid separated and was washed (with water, with dilute sodium carbonate, and again with water) and hydrolyzed with 150 ml of concentrated hydrochloric acid for six hours in a water bath. No attempt was made to isolate a crystalline azlactone. When the acid was added to this liquid, a crystalline precipitate formed which dissolved as the reaction mixture was heated. When hydrolysis was complete, the new precipitate that had formed was filtered off and the orange liquid was extracted with ether; the extract was dried and evaporated. The residual liquid was vacuum-distilled. 3-Methyl-2-oxovaleric acid had b.p. 62-63° (7 mm) and 72° (11 mm) (the literature gives 72-74° (11 mm) [15], 73° (10 mm) [20], 70-75° (11 mm) [21], 78-80° (12 mm) [22], 84° (15 mm) [23], and 90° (21 mm) [24]). The melting point of the white plate-like crystals was 36° (the literature gives 35° [23], 34.5-35.5° [15], 30° [21, 22], 38-40° for the optically active isomers of this α-keto acid [20]). The yield was 3.8 g. The sodium salt was prepared in the manner described above. The 2,4-dinitrophenylhydrazone melted at 168° (the literature gives 168-169° for the racemate [20] and 176° for either of the stereoisomers [20, 25]).

Of other methods of synthesizing 3-methyl-2-oxovaleric acid [16, 17, 20-25] Wieland's method [22] deserves special attention because of its comparative simplicity and the high yields obtained. Meister's method is also noteworthy [20]; it consists in the oxidative deamination of D-isoleucine or L-alloisoleucine by a preparation of D-amine oxidase from liver or the similar treatment of L-isoleucine or D-alloisoleucine by a preparation of L-amine oxidase from snake venom. In this case the L- and D-stereoisomers, respectively, are obtained.

SUMMARY

1. The condensation of aldehydes or ketones with N-acylglycines with subsequent hydrolysis of the resulting azlactones of 2-(acylamino)-3-alkyl(or aryl) acrylic acids must be regarded as another general method for the synthesis of α-keto acids.

2. The synthesis of 3-methyl-2-oxobutyric acid by condensation of acetone with hippuric acid and subsequent hydrolysis of the azlactone was repeated.

3. A new synthesis of 3-methyl-2-oxovaleric acid is described, namely, condensation of butanone with hippuric acid and subsequent hydrolysis of the resulting azlactone of 2-benzamido-3-methyl-2-pentenoic acid.

LITERATURE CITED

[1] K.L. Waters, Chem. Rev. 41, 585 (1947).

[2] J. Plochl, Ber. 2815 (1883).

[3] J. Buck and W. Ide, Organic Syntheses 2, 11, 1949.*

[4] H. Snyder, J. Buck and W. Ide, Organic Syntheses 2, 164, 1949.*

[5] A. Ellinger and Z. Matzuoka, Z. Physiol. Chem. 109, 259 (1920).

[6] C. Berg, W.H. Rose and C.S. Marvel, J. Biol. Chem. 85, 219 (1929).

[7] R. Herbst and D. Shemin, Organic Syntheses 2, 72, 1949.*

[8] M. Bergmann and F. Stern, Ann. 448, 20 (1926).

[9] R. Herbst and D. Shemin, Organic Syntheses 2, 518, 1949.*

[10] E. Erlenmeyer and E. Frŭstŭck, Ann. 284, 36 (1895).

[11] W.H. Perkin and J.L. Simonsen, Proc. Chem. Soc. 25, 164 (1909).

[12] G.R. Ramage and J.L. Simonsen, J. Chem. Soc. 1935, 532.

[13] M.M. Botvinik, M.A. Prokofyev and N.D. Zelinsky, Proc. Acad. Sci. USSR 30, 128 (1941).

[14] H. Carter, P. Handler and D.B. Melwill, J. Biol. Chem. 129, 359 (1939).

[15] J.T. Holden, R.B. Wildman and E.E. Snell, J. Biol. Chem. 191, 559 (1951).

[16] L. Bouveault and A. Wahl, Bull. Soc. Chim. 25, 1037 (1901).

[17] B. Rassow and R. Bauer, J. prakt. Chem. 80, 87 (1909).

[18] V.E. Price and L. Levintov, Biochem. Preparations 2, 22 (1952).

[19] K. Ramachandran and T.K. Walker, Arch. Biochem. Biophys. 31, 224 (1951).

[20] A. Meister, J. Biol. Chem. 190, 269 (1951).

[21] C. Neuberg and W.H. Peterson, Biochem. Z. 67, 38 (1914).

[22] T. Wieland, Ber. 81, 314 (1948).

[23] R. Loquin, Bull. Soc. Chim. 35, 964 (1906).

[24] A. Mebus, Monats. 26, 485 (1905).

[25] I.P. Greenstein, L. Levintov, C.G. Baker and J. White, J. Biol. Chem. 188, 647 (1951).

Received July 7, 1957

A.N. Bakh Institute of Biochemistry
Academy of Sciences, USSR

*Russian translation.

TELOMERIZATION OF PROPENE AND ETHYLENE WITH METHYL FORMATE

G.I. Nikishin, V.D. Vorobyev and A.D. Petrov

The homolytic telomerization of ethylene in presence of peroxide catalysts has been brought about in many cases with such telogens as alcohols [1], aldehydes [2], ketones [3], acids [4], silanes containing silicon-attached hydrogen [5], etc., and it has been particularly thoroughly studied for polyhalomethanes [6]. These reactions have resulted in the preparation of higher functional compounds with a normal carbon chain. The telomerization of propene has received much less study.

Urry and Huyser [7] showed that, in presence of tert-butyl peroxide, ethylene and methyl formate give a series of methyl esters ranging from propionic to tridecanoic. They carried out the reaction at 130° at an ethylene pressure of 30 atmos and a molar ratio of ester to peroxide of 10 : 0.061. Having before us the task of synthesizing acids having a branched carbon chain and their esters, we examined the telomerization of methyl formate with propene. We considered that it would be of interest to study also the reaction of ethylene with methyl formate at pressures higher than those used previously [7].

Reaction of propene with methyl formate was carried out at a pressure of 100 atmos, at 100°, with the proportions of ester : propene : tert-butyl peroxide = 1.5 : 4.6 : 0.11. It was found that in addition to telomerization:

$$n\,CH_2=CH-CH_3 + HC\!\!\begin{array}{l}\nearrow O\\ \searrow OCH_3\end{array} \rightarrow H(C_3H_6)_nC\!\!\begin{array}{l}\nearrow O\\ \searrow OCH_3\end{array}$$

polymerization of propene proceeded to a considerable extent, and it was very difficult to separate the ester products from the admixed hydrocarbons. The total ester content of the reaction mixture in various fractions over the boiling range 90-135° (4 mm) amounted to 20-40%. By hydrolysis of the individual fractions with alkali, the esters were converted into potassium salts of the acids, which were separated from the hydrocarbons and converted into silver salts. Analysis of the salts for silver showed that they were derivatives of butyric, heptanoic, and decanoic acids. Salts having silver contents corresponding to higher acids were also obtained, but we did not succeed in isolating them. The telomerization of ethylene was carried out at 200 atmos and 150°. Under these conditions no liquid products were formed. A paraffin-like substance was obtained which, according to elementary analysis and its ester and acid values, had an average molecular weight of the order of 1850.

EXPERIMENTAL

1. A mixture of 100 g (2.3 moles) of methyl formate, 320 ml (4.6 moles) of propene (commercial), and 10 g (0.09 mole) of tert-butyl peroxide was prepared in a cooled one-liter autoclave made of 1K18-N9T stainless steel. The autoclave was heated at 150° for eight hours; the initial pressure of propene at this temperature was 100 atmos. The product (30 g) boiled above 70°. The product from several experiments was fractionated through a column. The ester values of the fractions were determined by hydrolysis with 0.5 N alcoholic KOH. The hydrocarbons were separated, and after being treated with dilute sulfuric acid and ammonia the potassium salts were converted into the silver salts with 5% silver nitrate. Fraction I, b.p. 90-100° (n_D^{20} 1.4103; d_4^{20} 0.8171) and ester value 219, gave a silver salt containing 55.06% of silver; calculated for C_3H_7COOAg: 55.33% Ag. Fraction II, b.p. 175-195° (n_D^{20} 1.4376; d_4^{20} 0.8128) and ester value 73.10, gave a silver salt containing 43.64% of silver; calculated for $C_6H_{13}COOAg$: 44.75% Ag. Fraction III, b.p. 109-128° (4 mm) (n_D^{20} 1.4546; d_4^{20} 0.8544) and ester value 41.2, gave a silver salt containing 38.9% of silver; calculated for $C_9H_{19}COOAg$: 38.10% Ag.

2. A mixture of 126 g (2 moles) of methyl formate and 3 g (0.03 mole) of the peroxide was prepared in a one-liter autoclave cooled with solid carbon dioxide; ethylene was then passed in. The autoclave was heated at 150° for 10 hours. At this temperature the initial pressure of ethylene was 200 atmos. The product, amounting to 50 g, was a solid wax, insoluble in ether and alcohol and sparingly soluble in hexane. After being washed with ether and dried, the substance had m.p. 85-86°, and ester value (determined by boiling it with 0.5 N butanolic KOH) 29.11. The potassium salts of the acids, obtained by boiling the wax with alkali, were converted into acids, and the acid value of these was determined and found to be 30.55. Elementary analysis of wax (%): C 84.24; H 14.27. Molecular weight, calculated from the ester value, 1857, calculated from the acid number, 1836, which is close to that of the ester $H(CH_2CH_2)_{69}C(=O)OCH_3$, molecular weight 1855, C 84.16% and H 14.12%.

SUMMARY

1. When propene and methyl formate react in presence of tert-butyl peroxide, telomerization occurs with formation of methyl esters of higher acids; in addition the propene polymerizes with formation of hydrocarbons.

2. Reaction of methyl formate with ethylene gave methyl esters of acids of average molecular weight 1850.

LITERATURE CITED

[1] W.H. Urry, F. Stacey, E. Huyser and O. Juveland, J. Am. Chem. Soc. 76, 450 (1954).

[2] K. Ziegler, Brennst-Chem. 30, 181 (1949).

[3] W. Bunes, W.P. Fitzberuld and J.F. Nelson, Canadian Patent 507257; Abstract J. (Chem) 17110 (1956).

[4] J.R. Roland and J. Harmon, U.S. Patent 2433015; C.A. 42, 2268 (1948); D.D. Coffman, U.S. Patent 2433016; C.A. 42, 2456 (1948).

[5] A.N. Nesmeyanov, R.Kh. Freidlina and E. Ts. Chukovskaya, Proc. Acad. Sci. USSR 112, 271 (1957)•; 113, 120 (1957).•

[6] R.M. Joyce, W.E. Hanford and J. Harmon, J. Am. Chem. Soc. 70, 2529 (1948); J. Harmon, T.A. Ford, W.E. Hanford and R.M. Joyce, J. Am. Chem. Soc. 72, 2213 (1950); A.N. Nesmeyanov, Sh.A. Karapetyan and R.Kh. Freidlina, Proc. Acad. Sci. USSR 109, 791 (1956).•

[7] W.H. Urry and E.S. Huyser, J. Am. Chem. Soc. 75, 4877 (1953).

Received July 4, 1957

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

•Original Russian pagination. See C.B. translation.

CYANOETHYLATION OF METHYL- AND ETHYL-DICHLOROSILANES

A.D. Petrov and V.M. Vdovin

We first carried out the addition of a silane having silicon-attached hydrogen to acrylonitrile in the case of trichlorosilane [1]; the reaction was carried out in an autoclave in absence of solvents. At the same time we attempted to cyanoethylate also CH_3SiCl_2H and $C_2H_5SiCl_2H$ under the same conditions with the aid of Raney nickel, platinized charcoal, and platinized calcium carbonate. The yields of addition products were small, however, and the products were complex in composition because addition occurred not only at C=C, but also at C≡N. Extensive investigations were later published by Japanese workers [2, 3], who also cyanoethylated trichlorosilane; they showed that in glass ampoules this reaction gives good yields when various catalysts are used, in particular pyridine, and only the β-isomer $Cl_3SiCH_2CH_2CN$ is formed under these conditions. However, in a steel autoclave with the same catalysts these authors observed the formation of only the α-isomer $Cl_3SiCH(CH_3)CN$, and the use of polar solvents, in particular acetonitrile, increased the yield to 30%.

In this paper we report the preparation of $CH_3SiCl_2(CH_2CH_2CN)$ and $C_2H_5SiCl_2(CH_2CH_2CN)$, which we carried out under the following conditions. We used equivalent amounts of acrylonitrile and alkyldichlorosilane in acetonitrile solution with pyridine as catalyst. The reaction was carried out in an autoclave at 160-170°. In experiments with pyridine the yields of $CH_3SiCl_2(CH_2CH_2CN)$ were 6-12% on the amount of CH_3SiCl_2H taken for reaction and more than 60% on the amount that reacted. The structures of the methyl- and ethyl-dichlorosilylpropionitriles were confirmed by titration with 0.1 N NaOH. Both compounds required two equivalents of alkali, which indicated the β-isomer, since the α-isomer, like $Cl_3SiCH(CH_3)CN$, should undergo β-decomposition when hydrolyzed and so require three equivalents of alkali.

The formation of the β-isomer was confirmed also by conversion of our product by the action of three molecules of CH_3MgI into the ketone $(CH_3)_3SiCH_2CH_2COCH_3$, previously prepared both by us [4] and by Sommer [5]. It must be mentioned that a small amount, separable by distillation, of low-boiling α-isomer is formed also in this reaction, for by reaction of the low-boiling fraction with three molecules of CH_3MgI some $(CH_3)_3SiO$-$Si(CH_3)_3$ was isolated. By the use of platinized silica gel as catalyst, the yield of addition products rose to 40-50% on the amount of CH_3SiCl_2H taken for reaction. However, compounds were now formed which were richer in silicon and of higher boiling point, which indicates the addition of two and three molecules of dichloromethylsilane to one molecule of acrylonitrile, evidently as a result of the presence of the C≡N bond. We will point out also that the nature of the material and the cleanliness of the walls of the autoclave appear to have a substantial effect on the addition of silanes to acrylonitrile. This is evident from the fact that in the cyanoethylation of dichloromethylsilane in different autoclaves we obtained considerable variation in the yields of CH_3SiCl_2-(CH_2CH_2CN), and in the cyanoethylation of trichlorosilane by the procedure of the Japanese investigators [3] in a steel autoclave we unexpectedly obtained the β-isomer (in 9% yield) instead of the α-isomer. American chemists [6] have recently reported, though without giving their experimental data, thay they had succeeded in bringing about the addition of CH_3SiCl_2H to CH_2=CHCN and CH_2=$CHCOOCH_3$ and detected α- and β-addition products by the paramagnetic resonance method.

EXPERIMENTAL

Synthesis of $CH_3SiCl_2(CH_2CH_2CN)$. A mixture of 115 g of CH_3SiCl_2H, 60 g of CH_2=CHCN, and 8 g of pyridine in 200 ml of acetonitrile was placed in a one-liter rotating autoclave and heated. When a temperature of 168° had been attained, in 20 minutes the pressure fell from 15 atmos to 13.5 atmos. In further heating for six hours at 166-170° no further fall in pressure was noted. Dichloromethylsilane (89 g) and other reactants were

distilled off, and the residue was vacuum-fractionated. A fraction of b.p. 60-90° (8 mm)(23 g) was collected. Refractionation of this gave:

Fraction I, b.p. 106-111° (40 mm); 3.2 g
Fraction II, b.p. 111-113° (40 mm); 12 g
Fraction III, b.p. 113-131° (40 mm); 2 g
Fraction IV, b.p. 140-150° (3 mm); 2.3 g

Fraction II: n_D^{20} 1.4518; d_4^{20} 1.1722; calculated MR 38.62 [7]; found MR 38.66; found Si 16.50; 16.60%; calculated for $CH_3SiCl_2(CH_2CH_2CN)Si$ 16.69%.

In titration by Whitmore's method, a 0.9712-g sample required 113.8 ml of 0.1 N NaOH and a 0.6002-g sample required 70.6 ml of 0.1 N NaOH. The amounts calculated for $CH_3SiCl_2(CH_2CH_2CN)$ are 115.2 ml and 71.2 ml respectively. In the reaction of 8 g of Fraction II with CH_3MgI prepared from 20.2 g of CH_3I we obtained 4.5 g of $(CH_3)_3SiCH_2CH_2COCH_3$, b.p. 88-92°/(66 mm); n_D^{20} 1.4240; d_4^{20} 0.8309 (the literature gives b.p. 84° (65 mm); n_D^{20} 1.4228; d_4^{20} 0.8330 [5]; b.p. 81.5-83° (65 mm); n_D^{20} 1.4235; d_4^{20} 0.8325 [4]). Analysis of the lower-boiling Fraction I for Si gave the same results, but in this case reaction of 9.5 g of substance with 3 molecular proportions of CH_3MgI gave 0.8 g of $(CH_3)_3Si-O-Si(CH_3)_3$, b.p. 98-101° and n_D^{20} 1.3740, and 1.7 g of $(CH_3)_3SiCH_2CH_2COCH_3$, b.p. 89-92° (66 mm), n_D^{20} 1.4237. Analysis of Fraction IV gave Si 20.0, 20.3%. Calculated for $C_5H_{10}Si_2Cl_4N$ (product of the addition of two CH_3SiCl_2H molecules to $CH_2=CHCN$): Si 19.82%.

Synthesis of $C_2H_5SiCl_2[CH_2CH_2CN]$. Reaction between 200 g of $C_2H_5SiCl_2H$, 90 g of $CH_2=CHCN$ and 10 g of C_5H_5N was carried out under the same conditions. Two fractionations gave 12.9 g of a fraction of b.p. 122-124° (40 mm), n_D^{20} 1.4557; d_4^{20} 1.1561; calculated MR 43.13; found MR 42.79. Titration with 0.1 N NaOH gave 74.1 ml for a 0.6626-g sample and 65.6 ml for a 0.5300-g sample. The amounts calculated for $C_2H_5SiCl_2(CH_2CH_2CN)$ are 73.6 ml and 64.6 ml respectively. Found Si 15.62, 15.53%; calculated for $C_2H_5SiCl_2(CH_2CH_2CN)$ 15.35%.

When the reaction was carried out with 115 g of CH_3SiCl_2H, 60 g of $CH_2=CHCN$ and 0.3 g of 0.5% Pt on silica gel in 200 ml of acetonitrile, on the attainment of 170° there was a sharp fall in pressure from 15 to 9 atmos. Fractionation gave 12 g of a crystalline substance, m.p. 31.5° and b.p. 112° (16 mm), and other high-boiling substances (46 g). Found Si 20.1-20.4%. For $C_5H_{10}Si_2Cl_4N$ (product of the addition of two CH_3SiCl_2H molecules to acrylonitrile), calculated Si 19.82%. No $CH_3SiCl_2(CH_2CH_2CN)$ was found. When these reactions were carried out under the same conditions and with the same relative amounts of reactants, but in absence of solvent (acetonitrile), then both in the steel autoclave and in the sealed ampoules no appreciable amounts of high-boiling silicon compounds could be detected.

Reaction between 100 g of $HSiCl_3$ and 48 g of $CH_2=CHCN$ in 200 ml of acetonitrile in presence of 10 g of pyridine gave 14 g of a fraction of b.p. 75-116° (40 mm). Fractionation gave a small amount of a liquid, b.p. 96-98° (41.5 mm) (α-isomer). The main product was the fraction of b.p. 117-118° (41 mm) and m.p. 33-34°. A mixture melting point test of this substance with $Cl_3SiCH_2CH_2CN$ obtained by us by direct synthesis [4], showed no depression. All experiments were carried out in EYa1-T steel autoclaves.

SUMMARY

By the condensation of methyl- and ethyl-dichlorosilanes with acrylonitrile in acetonitrile in presence of pyridine as catalyst, 3-(dichloromethylsilyl)propionitrile and 3-(dichloroethylsilyl)propionitrile were synthesized.

LITERATURE CITED

[1] A.D. Petrov, V.F. Mironov and V.M. Vdovin, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 257.•

[2] B.Y. Shunichi Nazakura and Shiro Konotsune, Bull. Chem. Soc. Japan 29, No. 3, 323.

[3] B.Y. Shunichi Nazakura and Shiro Konotsune, Bull. Chem. Soc. Japan 29, No. 3, 326.

[4] A.D. Petrov, S.I. Sadykh-Zade and V.M. Vdovin, Proc. Acad. Sci. USSR 100, No. 4, 711 (1955).

•Original Russian pagination. See C.B. translation.

[5] H. Sommer and S. Nelson, J. Am. Chem. Soc. 73, 5130 (1951).

[6] C. Goodman, R. Silverstein and J. Schoolery, J. Am. Chem. Soc. 78, 4493 (1956).

[7] R.L. Warrick, J. Am. Chem. Soc. 68, 2455 (1946).

Received July 5, 1957

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

ORGANOMAGNESIUM SYNTHESIS OF VINYL COMPOUNDS OF SILICON, GERMANIUM AND TIN

A.D. Petrov and V.F. Mironov

The first compound of this group $(C_2H_5)_3SiCH=CH_2$ was prepared [1] by the chlorination of tetraethylsilane to $CH_3ClCHSi(C_2H_5)_3$ and the dehydrochlorination of this with alcoholic alkali. This method of synthesizing vinyl compounds of silicon (chlorination-dehydrochlorination) was later extended to other organosilicon compounds, in particular to $C_2H_5SiCl_3$, with the use of other dehydrochlorinating agents, quinoline and aluminum chloride [2]. In a similar way we recently synthesized trichlorovinylgermane [3]:

$$C_2H_5GeCl_3 \xrightarrow{SO_2Cl_2} ClCH_2CH_2GeCl_3 \xrightarrow{\text{quinoline}} CH_2=CHGeCl_3.$$

This method, however, though satisfactory for vinylsilanes, is not very convenient for germanium owing to the low yields obtained, and it will probably be almost ineffective in the case of tin. For these compounds the direct method is still less satisfactory, since in the reaction of vinyl chloride on alloys of copper with silicon* and with germanium [3], vinyl derivatives of these elements are formed in negligible yield. The addition of $HSiCl_3$ and $RSiHCl_2$ to acetylene under certain conditions [6-9] is not, according to our results, a convenient laboratory preparative method for the preparation of vinylsilicon compounds.

Moreover, it must be pointed out that all of the above-mentioned methods are suitable only for the synthesis of monovinyl derivatives of silicon or germanium. For the synthesis of di- and poly-vinylsilanes, both Kanazashi [10] and we [11] have used the condensation of chlorosilanes with vinyl chloride in presence of sodium:

$$R_nSiCl_{4-n} + 4(4-n)\,CH_2=CHCl \xrightarrow{Na} R_nSi(CH=CH_2)_{4-n}.$$

Although dimethyldivinylsilane is then formed in about 20% yield, we have not yet succeeded in synthesizing $(C_2H_5)_2Si(CH=CH_2)_2$ by this method [12].

The introduction by Normant [13] of an excellent method of synthesizing the Grignard reagent from vinyl bromide or chloride in a tetrahydrofuran medium prompted us to investigate the possibility of condensing this reagent with alkylchlorosilanes, -germanes, and -stannanes. It was found that both mono- and polyvinyl derivatives of silicon, germanium, and tin can be synthesized by this method in high yield, which makes this universal synthesis undoubtedly the most convenient. Below we describe the conditions for the synthesis of some of these compounds.

EXPERIMENTAL**

Triethylvinylstannane $(C_2H_5)_3SnCH=CH_2$.*** Ethyl bromide (0.5 g) was added to 11 g of magnesium in

*This observation is in accord with those of Hurd [4], but contradicts the statements of Shostakovsky and Kochkin [5].

**N.G. Maksimova took part in the experimental work.

***We became aware of the synthesis of this compound by Sejferth and Stone [14] only after the present work had been completed.

50 ml of tetrahydrofuran (distilled over sodium). When reaction was complete, a solution of 50 g of vinyl bromide in 100 ml of tetrahydrofuran was added. To the CH_2=CHMgBr so prepared, 92 ml of chlorotriethylstannane [15] was added: much heat was evolved and it was necessary to cool the flask. On the next day tetrahydrofuran was distilled from the flask and the residue was heated in a boiling water bath for two hours. Ether (200 ml) was added, and the contents of the flask were decomposed with water. The organic layer and ether extracts of the aqueous layer were combined and dried over calcium chloride. Ether was distilled off, and the residue was fractionated through a column. The product, amounting to 70 g (79%), was triethylvinylstannane, b.p. 174-175°; n_D^{20} 1.4780; d_4^{20} 1.2133; found MR 54.87; calculated MR 54.34.

Found %: C 41.36, 41.12; H 7.67, 7.73; Sn 51.27. $C_8H_{18}Sn$. Calculated %: C 41.25; H 7.79; Sn 50.95.

Ethyldivinylsilane $(C_2H_5)HSi(CH=CH_2)_2$. A solution of 90 g of vinyl bromide in 100 ml of tetrahydrofuran was added to 20.5 g of magnesium in 125 ml of tetrahydrofuran. To the resulting CH_2=CHMgBr, 50 g of $(C_2H_5)HSiCl_2$ was added. On the next day, boiling was continued for six hours. After the usual treatment, fractionation through a column gave 10.5 g (22.2%) of ethyldivinylsilane, b.p. 93-94.6°; n_D^{20} 1.4305; d_4^{20} 0.7559; found MR 38.40; calculated MR 38.71. A polymer (29 g) remained in the flask.

Found %: C 64.29, 64.16; H 10.71, 10.71; Si 24.77, 25.20. $C_6H_{12}Si$. Calculated %: C 64.20; H 10.77; Si 25.02.

Diethyldivinylgermane $(C_2H_5)_2Ge(CH=CH_2)_2$. Reaction between 18 g of magnesium in 125 ml of tetrahydrofuran and 80 g of vinyl bromide in 100 ml of tetrahydrofuran gave CH_2=CHMgBr, to which 69 g of $(C_2H_5)_2GeCl_2$ was added. On the next day tetrahydrofuran was distilled off and the residue was heated in a water bath for five hours. The usual treatment gave 35 g (55%) of diethyldivinylgermane, b.p. 149.8°; n_D^{20} 1.4575; d_4^{20} 1.0193.

Found %: C 51.95, 51.84; H 8.47, 8.48; Ge 39.28, 39.21. $C_8H_{16}Ge$. Calculated %: C 51.99; H 8.72; Ge 39.28.

Under similar conditions we synthesized $(C_2H_5)_2Si(CH=CH_2)_2$; $C_2H_5Si(CH=CH_2)_3$; $CH_3Si(CH=CH_2)_3$; $(CH_3)_3SnCH=CH_2$; $(C_2H_5)Ge(CH=CH_2)_3$; $(C_6H_5)_2Si(CH=CH_2)$; $C_6H_5CH_3Si(CH=CH_2)_2$; $C_6H_5Si(CH=CH_2)_3$.

It should be mentioned that, in the first place [12], working with tetrahydrofuran prepared from furaldehyde obtained in the wood-processing industry, we were unable to obtain diethyldivinylsilane with the aid of Normant's reagent.

SUMMARY

It was shown that condensation of Normant's reagent (CH_2=CHMgBr) with alkylchlorosilanes, -germanes, and -stannanes results in the synthesis of vinyl derivatives of silanes, germanes, and stannanes containing one, two, or three, vinyl radicals.

LITERATURE CITED

[1] S.N. Ushakov and A.M. Itenberg, J. Gen. Chem. 7, 2495 (1937).

[2] A.D. Petrov, V.F. Mironov and D. Mashantsker, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 550.*

[3] A.D. Petrov, V.F. Mironov and I.E. Dolgy, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1146.*

[4] D.T. Hurd, J. Am. Chem. Soc. 67, 1813 (1945).

[5] M.F. Shostakovsky and D.A. Kochkin, Bull. Acad. Sci. USSR, div. chem. sci. 1954, 174.*

[6] G.H. Wagner, U.S. Patent 2637738; C.A. 48, 8254 (1954); C.A. 46, 8894 (1952).

[7] C.L. Agre and W. Hilling, J. Am. Chem. Soc. 74, 3895 (1952).

*Original Russian pagination. See C.B. translation.

[8] M.F. Shostakovsky and D.A. Kochkin, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1150.•

[9] M.F. Shostakovsky and D.A. Kochkin, Proc. Acad. Sci. USSR 109, 113 (1956).•

[10] M. Kanazashi, Bull. Chem. Soc. Japan 26, No. 9, 493 (1953).

[11] A.D. Petrov, V.F. Mironov and V.G. Glukhovtsev, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 461.•

[12] A.D. Petrov, V.F. Mironov and V.G. Glukhovtsev, J. Gen. Chem. 27, 1535 (1957).•

[13] H. Normant, Bull. Soc. Chim. France 5, 728 (1957).

[14] D. Sejferth and F.G.A. Stone, J. Am. Chem. Soc. 79, 515 (1957).

[15] K.A. Kocheshkov, J. Gen. Chem. 4, 1359 (1934).

Received July 5, 1957

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

•Original Russian pagination. See C.B. translation.

RELATIVE EFFICIENCIES OF SILICON–COPPER AND SILICON–NICKEL ALLOYS IN THE DIRECT SYNTHESIS OF CHLOROVINYLSILANES

M.F. Shostakovsky, E.M. Savitsky, D.A. Kochkin and L.V. Musatova

It has been shown previously that chlorovinylsilanes can be prepared by passing vinyl chloride over a silicon-copper alloy [1, 2]. There is also a patent [3] concerning the use of Group V-VIII metals as activators for the silicon-copper alloy. Later, more detailed investigations, reported below, showed that the relative amounts of the alloy components and the reaction conditions are of great importance. When the alloy described in our previous communication [1] was analyzed more carefully, it was shown that it contained 50% of silicon, 49.2% of copper, and 0.4% of aluminum. Silicon-copper alloys containing less than 50% of copper were found to be not very effective for the preparation of chlorovinylsilanes. We investigated also silicon alloys containing various other metals, i.e., chromium, manganese, molybdenum, cobalt, tungsten, magnesium, aluminum, nickel, and mischmetall. All experiments were carried out at temperatures of up to 700°.

For all metals other than nickel and copper, negative results were obtained. From the results on the synthesis (see table) it follows that silicon-nickel is more active than silicon-copper. The best results in the synthesis of chlorovinylsilanes were obtained with a silicon-nickel alloy containing 80% of silicon and 15% of nickel. Silicon-nickel alloys of higher nickel content bring about the formation of a considerable amount of decomposition products of vinyl chloride. Thus, with an alloy of 50% silicon and 50% nickel the main reaction product was silicon tetrachloride. In this case the catalyst was rapidly poisoned. For practical purposes the synthesis became ineffective after 25-30 hours. It must be supposed that synthesis in a suspended layer of catalyst, i.e., under conditions of considerably increased effective catalyst surface and a more favorable temperature schedule, could be carried out more effectively.

Fractionation through a column showed that the reaction products contained trichlorovinyl- and dichlorodivinylsilanes and the following by-products: trichlorosilane (up to 30%), silicon tetrachloride (up to 40-50%), dichloroethylsilane (1.5%), trichloroethylsilane (3-4%), and high-boiling products the composition of which we have not yet established.

1. $2CH_2=CHCl + Si \rightarrow (CH_2=CH)_2SiCl_2$
2. $3CH_2=CHCl + Si \rightarrow CH_2=CHSiCl_3 + 4C + 3H_2$
3. $3CH_2=CHCl + 2Si \rightarrow CH_2=CHSiHCl_2 + CH_2=CHSiH_2Cl + 2C$
4. $4CH_2=CHCl + Si \rightarrow SiCl_4 + 8C + CH_2$
5. $3CH_2=CHCl + Si \rightarrow HSiCl_3 + 6C + 4H_2$
6. $CH_2=CHSiHCl_2 + H_2 \rightarrow C_2H_5SiHCl_2$
7. $CH_2=CHSiCl_3 + H_2 \rightarrow C_2H_5SiCl_3$

The most satisfactory reactions from the point of view of the utilization of the vinyl chloride are those giving dichlorodivinyl- and trichlorovinylsilanes [Equations (1) and (2)]. The formation of dichloroethylsilane [Equation (6)] and trichloroethylsilane [Equation (7)] can be explained by the hydrogenation of the corresponding chlorovinylsilanes. Hydrogen is formed as a result of the pyrolysis of the reaction products and of the original vinyl chloride.

EXPERIMENTAL

Direct synthesis of chlorovinylsilanes in presence of an 80:20 silicon-nickel alloy. The alloy* (450 g) in the form of lumps or of coarse powder was placed in a stainless steel catalysis tube, 600 mm in length and 42 mm in diameter, fitted with thermocouple, flow meter, receiver, condenser, and trap cooled with solid carbon dioxide, and acetone. In order to attain a more uniform distribution, short lengths of hard-glass tube were added. The alloy was dried in a stream of nitrogen at 300° for two hours. Vinyl chloride was passed at a rate of 12-15 g per hour at 420-450°. In the course of 61 hours, 689 g of vinyl chloride was passed and 176.0 g of liquid reaction products was obtained. It was fractionated through a column (20 theoretical plates).

The following fractions were obtained:

Fraction I, 41.2 g (23.4% by weight), b.p. 31.32°; found Cl 78.34, 78.25%; d_4^{20} 1.3428. Fraction I consisted mainly of trichlorosilane $HSiCl_3$. The literature gives b.p. 31.8° (760 mm), d_4^{20} 1.3438. Calculated for $HSiCl_3$ 78.51% Cl.

Fraction II, 50.2 g (28.5%), b.p. 55-57°; found Cl 83.18, 83.00%, which corresponds to silicon tetrachloride.

Fraction III, 2.6 g (1.5%), b.p. 62-82°; found Cl 55.00, 54.85%; d_4^{20} 1.077, corresponded to dichloroethylsilane. The literature gives b.p. 74.5° (752 mm) d_4^{20} 1.0849. Calculated for $C_2H_5SiHCl_2$ 55.0% Cl.

Fraction IV, 26.0 g (14.8%), b.p. 88-95°; found Cl 65.42, 65.27%; d_4^{20} 1.2588, was trichlorovinylsilane. The literature gives b.p. 92° (742 mm); d_4^{20} 1.2650 [4].

Fraction V, 10.7 g (6.1%), b.p. 97-103°; found Cl 65.0, 64.78%; d_4^{20} 1.2269, was trichloroethylsilane. The literature gives b.p. 97-103° (760 mm); d_4^{20} 1.2388.

Fraction VII, 5.6 g (3.2%), b.p. 113-120°; found Cl 46.05, 46.01%; d_4^{20} 1.0800, contained dichlorodivinylsilane. The literature gives b.p. 118-119° (754 mm); d_4^{20} 1.0813 [1]; calculated for $(C_2H_3)_4SiCl_2$ 46.30% Cl.

Fraction VIII, 1.8 g (1.2%), b.p. 127-130°; found Cl 44.81, 44.91%; d_4^{20} 1.131, was dichlorodiethylsilane. The literature gives b.p. 128-130° (760 mm); d_4^{15} 1.106; calculated for $(C_2H_5)_2SiCl_2$ 45.15% Cl.

Fraction IX, 27.5 g (15.6%), was the high-boiling residue, b.p. above 130°.

The results on the synthesis of chlorovinylsilanes are given in the table, which states the optimum temperature, the time (hours) and the rate of passage of vinyl chloride. Under these conditions the synthesis was at its highest efficiency. Thus, continuation of the process with the above-specified alloy beyond a period of 61 hours did not give very satisfactory results even when the temperature was raised and the rate of passage of vinyl chloride was changed. The alloy was converted into a black friable mass of high carbon content. The table gives the results of syntheses in presence of other alloys, the procedure being as indicated above.

TABLE

Results of the Direct Synthesis of Chlorovinylsilanes in Presence of Copper and Nickel Alloys of Silicon (rate of passage of vinyl chloride 12-15 g/hour; amount of alloy 450 g)

Comp. of alloy (%)			Temp. of synthesis (°C)	Yield of reaction products (g)	Duration of synthesis (hrs)	Composition of reaction products (%)							
Si	Ni	Cu				$HSiCl_3$	$SiCl_4$	$C_2H_5SiHCl_2$	$CH_2=CHSiCl_3$	$C_2H_5SiCl_3$	$C_2H_5SiCl_3$ and $(CH_2=CH)_2SiCl_2$	$CH_2=CH)_2SiCl_2$	High-boiling residue, b.p. above 120°
80	15	—	420—430	176.0	61.0	23.4	28.5	1.5	14.8	6.1	0.8	3.2	15.6
70	30	—	370—420	152.0	41.0	13.7	52.1	2.2	8.0	4.5	0.9	1.3	15.7
80	50	—	300—360	171.0	20.5	21.6	40.1	3.6	3.3	6.5	1.2	2.8	13.7
50	—	50	470—490	112.0	53.0	20.0	40.0	6.4	16.0	1.6	1.3	—	12.2
80	10	10	420—450	21.0	14.5	13.5	35.4	2 8	11.0	3.9	0.9	—	10.9

*The alloys were prepared by Yu.G. Kolonin.

SUMMARY

1. It was shown that silicon-nickel alloys are more effective than silicon-copper alloys in the direct synthesis of chlorovinylsilanes.

2. It was shown that silicon-nickel alloys containing 15% or more of nickel are the most satisfactory.

LITERATURE CITED

[1] M.F. Shostakovsky and D.A. Kochkin, Bull. Acad. Sci. USSR, div. chem. sci. 1954, 174.*

[2] D.H. Hurd, J. Am. Chem. Soc. 67, 1813 (1945).

[3] Nitsche, Federated German Republic Patent 921566 (1954); Abstract J. (Chem.) 5747, No. 2 (1957); C. 1955, 126, No. 13, 3005.

[4] M.F. Shostakovsky and D.A. Kochkin, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1150.*

Received August 13, 1957

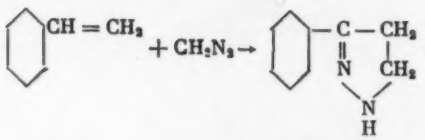
N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

*Original Russian pagination. See C.B. translation.

PRODUCTS OF THE ADDITION OF DIAZOMETHANE TO UNSATURATED COMPOUNDS

V.V. Korshak and V.A. Sergeev

The reaction of diazomethane with olefine results in the formation of various pyrazolines [1, 2]. We prepared pyrazolines by the addition of diazomethane to styrene, methyl acrylate, methyl methacrylate, ethylene diacrylate, and ethylene dimethacrylate. Addition of diazomethane to styrene gave 3-phenyl-2-pyrazoline:



3-phenyl-2-pyrazoline

3-Phenyl-2-pyrazoline (m.p. 45-47°) was characterized as its hydrochloride and N-nitroso derivative (m.p. 151-153°), and it was found to be identical with the pyrazoline obtained by Auwers and Heimke [3] from 3-chloropropiophenone and hydrazine hydrate. In this way we showed the incorrectness of the results of Oliveri-Mandala [4], who found that the addition of diazomethane to styrene gave 4-phenyl-2-pyrazoline.

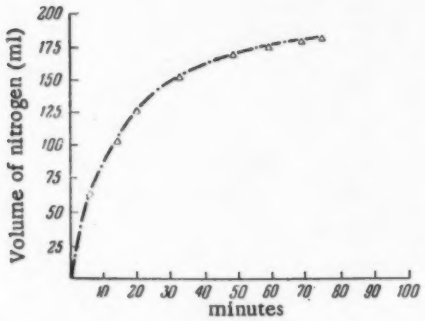


Fig. 1. Liberation of nitrogen in the decomposition of the ethylene ester of 2-pyrazoline-3-carboxylic acid at 179° (amount of substance taken 1.13 g).

The products of the addition of diazomethane to ethylene diacrylate and to ethylene dimethacrylate have not been described in the literature. Table 1 gives the temperatures at which these pyrazolines begin to decompose.

The kinetics of the decomposition of the ethylene ester of 2-pyrazoline-3-carboxylic acid at 179° are shown in Figure 1. Decomposition proceeds as a unimolecular reaction rate constant $k = 0.026$ minute^{-1}.

As there are references [5] in the literature to the possibility of using pyrazolines as initiators for free-radical polymerization, we investigated the initiating powers of the pyrazolines obtained.

The ability of pyrazolines to initiate free-radical polymerization was examined for monomers such as styrene, methyl acrylate, and methyl methacrylate. Table 2 gives the results of the polymerization of styrene at 120-121° for seven hours in presence of various amounts of the ethylene ester of 5-methyl-2-pyrazoline-5-carboxylic acid.

As will be seen from Table 2, the rate of polymerization remains the same as that of the control sample. Benzene-soluble polystyrene was obtained, and no trace of insoluble three-dimensional polymer could be found. The polymerization of styrene was investigated further at 80° in presence of 0.5% of the pyrazolines that we had obtained and also of diazoacetic ester, diazomethane, and benzoyl peroxide.

TABLE 1

Temperatures at Which Pyrazolines Begin to Decompose

Pyrazoline	Temperature at which decomposition starts (°C)
Methyl 5-methyl-2-pyrazoline-5-carboxylate	98
Methyl 3,5-dimethyl-2-pyrazoline-5-carboxylate	111
Ethylene bis(2-pyrazoline-3-carboxylate)	173
Ethylene bis(5-methyl-2-pyrazoline-5-carboxylate)	95

TABLE 2

Concentration of ethylene bis(5-methyl-2-pyrazoline-5-carboxylate)	0.0	0.15	0.31	0.61	1.23
Conversion (%)	59.0	61.2	62.5	60.5	59.0

Figure 2 shows that the rate of polymerization of styrene in presence of pyrazolines remains almost the same as the rate of thermal polymerization. These substances, therefore are not capable of initiating free-radical polymerization of styrene. For the polymerization of methyl acrylate and methyl methacrylate the pyrazolines even behaved as inhibitors, for in their presence no solid polymer could be isolated even after 28 hours.

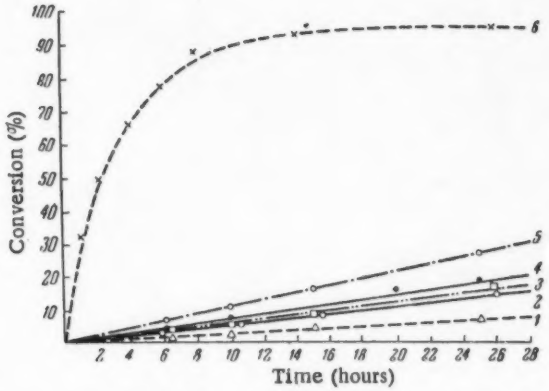


Fig. 2. Kinetics of the polymerization of styrene at 80° in presence of 0.5% of 1) ethylene bis(3-methyl-2-pyrazoline-3-carboxylate); 2) 3-phenyl-2-pyrazoline; 3) diazoacetic ester; 4) no addition; 5) ethylene bis(2-pyrazoline-5-carboxylate); 6) benzoyl peroxide.

SUMMARY

1. It was shown that reaction between diazomethane and styrene results in the formation of 3-phenyl-2-pyrazoline.

2. Products of the addition of diazomethane to the ethylene esters of acrylic and methacrylic acids were prepared.

3. The kinetics of the decomposition of the ethylene esters of 2-pyrazoline-3-carboxylic and 5-methyl-2-pyrazoline-5-carboxylic acids were studied.

LITERATURE CITED

[1] B. Eistert, in the collection: New Methods of Preparative Organic Chemistry (Foreign Lit. Press, Moscow, 1950), p. 116 [Russian translation].

[2] S.M. Gurvich and A.P. Terentyev, Collection of Papers on Gen. Chem. Vol. 1 (Izd. AN SSSR, Leningrad, 1953), p. 409 [in Russian].

[3] K. Auwers and P. Heimke, Ann. 458, 207 (1927).

[4] E. Oliveri-Mandala, Cazz. 40, 1, 117 (1910).

[5] J. Breitenbach and A. Kaster, Monats. 84, 645 (1953).

Received May 28, 1957

Institute of Heteroorganic Chemistry
Academy of Sciences, USSR

FREE-RADICAL MECHANISM OF THE THERMODEGRADATION OF CELLULOSE AND FORMATION OF LEVOGLUCOSAN*

A.M. Pakhomov

The mechanism which, until now, has been most generally favored for the formation of levoglucosan in the thermodegradation of cellulose in a vacuum [1] may be represented as follows:

$$\text{Cellulose} \xrightarrow{+H_2O} \text{glucose} \xrightarrow{-H_2O} \text{levoglucosan}$$

We have already shown [2] that the thermodegradation of cellulose in a vacuum proceeds mainly by breakdown at the 1,4-glucosidic linkages.

In the course of further investigation of the mechanism of the thermodegradation of cellulose in a vacuum and the formation of levoglucosan we suggested [3] that the formation of levoglucosan proceeds by a free-radical mechanism:

$$\text{Cellulose} \longrightarrow \text{free radicals} \longrightarrow \text{levoglucosan}$$

This suggestion is in accord with the experimental data. Free structural units of cellulose (radicals) of this sort can be formed by the breakdown of 1,4-glucosidic linkages. It ceases to be necessary to assume an intermediate stage, i.e., the formation of glucose (which is not in accord with experiment [2]). We now have an explanation for the transposition of bonds in the formation of levoglucosan from cellulose. On the basis of a free-radical mechanism we can picture the formation of 1,6-anhydro-β-D-glucofuranose [4] and the formation of 2,3,6-tri-0-methyl-1,4-anhydro-β-D-glucopyranose in the thermodegradation of trimethylcellulose [5].

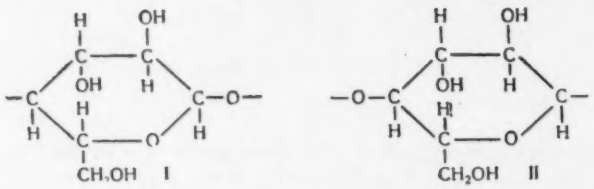
Moreover, the free-radical mechanism of the thermodegradation of cellulose is highly consistent with the available data on the chemistry of free radicals in the thermal decomposition of both simple and complex stable organic compounds [6]. In macromolecular heterochain compounds the weakest link in the chain is generally the bond between carbon and the hetero atom [7]. This has been noted for polyoxymethylene [8], polyethylene sebacate, polydiethylene sebacate [8], and other polymers. The high yield of levoglucosan and its structure leads us to the conclusion that the weakest link in the cellulose molecule is the 1,4-glucosidic linkage.

On analogy with available data on the behavior of macromolecular compounds such as rubber and the like, which give mainly cyclic compounds at low temperatures (180-350°) and more highly degraded products at high temperatures [10-12], we may suppose that, in the breakdown of a cellulose molecule at 1,4-glucosidic linkages, in the first place large radicals are formed, and these can then break down further in two ways. There may be intraradical transpositions of atoms in the terminal structural unit of cellulose carrying the free bond with simultaneous breakaway of the radical, mutual saturation of free valences, and formation of the stable neutral molecule of levoglucosan. Similar intraradical transpositions then occur with the next structural unit, and so on. The other way includes initial breakaway of the terminal structural unit, formation of a diradical, and its further isomerization into levoglucosan.

*This work was the subject of a report to an open colloquium of the Laboratory of Natural Macromolecular Compounds of the Institute of Organic Chemistry of the Academy of Sciences of the USSR held in 1955.

It is evident that this is the way in which trimethylcellulose behaves when heated in a vacuum. The trimethylcellulose molecule breaks at 1,4-linkages and, as the hydroxy groups of the original molecule are replaced by methoxy groups, the radicals formed give stable neutral molecules of 2,3,6-tri-O-methyl-1,4-anhydro-β-D-glucopyranose as a result of the mutual saturation of free valences in the 1- and 4-positions. In any case, it appears that a necessary condition for the formation of levoglucosan in the thermal decomposition of carbohydrates is the formation of radicals having free valences in the 1- or 4-positions and having the chemical composition of levoglucosan. If this condition is not fulfilled, the formation of levoglucosan is not very probable.

As already stated, one possible way in which large radicals may break down results in the formation of diradicals. In this case diradicals (I) and (II) may be formed:



Data in the literature [6] show that diradicals may undergo various further chemical transformations, but if a radical,or particularly a diradical, is an isomer of a neutral molecule, isomerization to a stable molecule will be the primary process. Diradicals, therefore,have an extremely short life and are therefore rarely able to initiate chain reactions [13].

For the formation of levoglucosan from the diradical (I) it is necessary to assume the transposition of a hydroxyl from C-6 to C-4 with mutual saturation of the free valence of the hydroxy group on C-1 and the free valence on C-6. In the formation of levoglucosan from the diradical (II) it is necessary to assume saturation of the free valence of the oxygen on C-4 with hydrogen and the formation of an oxygen bridge between C-1 and C-6. According to Reeves [14], the spatial structure of levoglucosan is such that the formation of an oxygen bridge in the 1,6-position should be sterically hindered, since the distance between these atoms is small and they are disposed on the same side of the plane of the pyranose ring.

In addition to these main transformations of the diradicals into levoglucosan, to a slight extent other isomerizations are also possible. Thus, by the opening of the 1,5-oxygen bridge in the diradical (II), 1,6-anhydro-β-D-glucofuranose can readily be formed.

The proposed scheme is consistent with other existing suggestions concerning the regularities observed in the breakdown of large molecules and the formation of cyclic compounds [15].

SUMMARY

1. A free-radical mechanism is suggested for the thermodegradation of cellulose in a vacuum and the formation of levoglucosan.

2. It is shown that the free-radical mechanism is consistent with the existing experimental data on the chemistry of free radicals.

LITERATURE CITED

[1] J.C. Irvine and J.W.H. Oldham, J. Chem. Soc. 119, 1744 (1921).

[2] V.I. Ivanov, O.P. Golova and A.M. Pakhomov, Bull. Acad. Sci. USSR, div. chem. sci. 1956, 1266.*

[3] O.P. Golova, V.I. Ivanov, A.M. Pakhomov, E.A. Andrievskaya and R.G. Krylova, Summaries of Papers read at Tenth Conference on General Questions on the Chemistry and Physics of Macromolecular Compounds (Izd. AN SSSR, Moscow, 1956), p. 68**; O.P. Golova, A.M. Pakhomov and E.A. Andrievskaya, Proc. Acad. Sci. USSR 112, No. 3 (1957).***

*Original Russian pagination. See C.B. translation.

**In Russian.

***See C.B. translation.

[4] R.G. Dimler, H.A. Davis and G.E. Hilbert, J. Am. Chem. Soc. 68, 1377 (1946).

[5] A.M. Pakhomov, O.P. Golova and I.I. Nikolaeva, Bull. Acad. Sci. USSR, div. chem. sci. 1957, 521.*

[6] F.O. Rice and K.K. Rice, The Aliphatic Free Radicles [Russian translation] (ONTI, Leningrad, 1937); W.A. Waters, The Chemistry of Free Radicals [Russian translation] (Foreign Lit. Press, Moscow, 1948); N.N. Semenov, Progr. Chem. 20, 673 (1951).

[7] V.V. Korshak, Chemistry of Macromolecular Compounds (Izd. AN SSSR, Moscow, 1950), pp. 97-98.**

[8] A.M. Butlerov, Ann. Chem. Pharm. 111, 242 (1859).

[9] P.P. Shorygin and E.K. Smolyaninova, Syntheses of Perfumes (Food Industry Press, Moscow, 1938), p. 178.**

[10] V.V. Korshak, Chemistry of Macromolecular Compounds (Izd. AN SSSR, Moscow, 1950), p. 103.**

[11] V.V. Korshak, Chemistry of Macromolecular Compounds (Izd. AN SSSR, Moscow, 1950), p. 96.**

[12] Th. Midgley and A.L. Henne, J. Am. Chem. Soc. 51, 1215 (1929).

[13] N.N. Semenov, Progr. Chem. 20, 673 (1951).

[14] R.E. Reeves, J. Am. Chem. Soc. 71, 2116 (1949).

[15] O.F. Rice and K.K. Rice, The Aliphatic Free Radicles [Russian translation] (ONTI, Leningrad, 1937), p. 137.

Received July 2, 1957

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR

*Original Russian pagination. See C.B. translation.

**In Russian.

TRANSFORMATIONS OF CELLULOSE AT ELEVATED TEMPERATURES

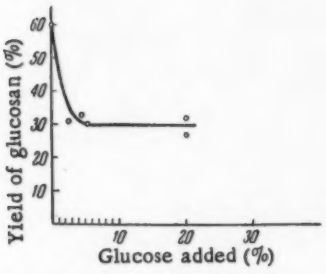
COMMUNICATION 6. EFFECT OF ADDITIONS OF GLUCOSE ON THE FORMATION OF LEVOGLUCOSAN IN THE VACUUM THERMODEGRADATION OF CELLULOSE

O.P. Golova, A.M. Pakhomov and E.A. Andrievskaya

Our previous investigation of the vacuum thermodegradation of cellulose led us to some interesting observations on the ways in which the yield of levoglucosan is affected by the physical structure of the cellulose [1] and the chain length of its macromolecule [2]. We showed also that levoglucosan is formed in low yield from regenerated cellulose, i.e., from readily hydrolyzed cellulose [1]. These investigations suggested that glucose has a specific unfavorable effect on the formation of levoglucosan. In order to verify this suggestion we investigated the effect of additions of α- and β-glucose on the formation of levoglucosan.

EXPERIMENTAL

The thermodegradation was carried out under the optimum conditions which we have used previously for the preparation of levoglucosan from cellulose [1]. Glucose was introduced into the sphere of reaction in two ways. At first the thermodegradation of cellulose was carried out in a stream of decomposition products of glucose obtained by heating glucose in a separate vessel. Under these conditions no reduction in the yield of levoglucosan was noted. This could be explained by an inadequate period of contact with the thermodecomposition products of glucose as a result of the presence of a high vacuum, and also by the shortness of the period during which these products exist in an active form. In later experiments, therefore, glucose was introduced directly into the cellulose preparation: 2-20% of glucose was mixed with the loose cellulose and the mixture was briquetted. In this case we observed an appreciable reduction in the amount of levoglucosan formed. As will be seen from the figure, the yield of levoglucosan fell to 30% on the cellulose taken, irrespective of the amount of glucose introduced and its configuration (α- or β-glucose).



Effect of addition of glucose to cellulose on yield of levoglucosan.

In explanation of this phenomenon it may be supposed that the lowering of the yield of levoglucosan is due to the retarding effect of the very active fragments of the glucose molecule on the formation of levoglucosan. The mechanism can be elucidated only after a detailed study of the kinetics of thermodegradation in presence of glucose.

SUMMARY

The presence of 2-20% of glucose in cellulose during its thermal degradation results in a reduction in the yield of levoglucosan from 55-60% to 30%.

LITERATURE CITED

[1] O.P. Golova, A.M. Pakhomov and E.A. Andrievskaya, Proc. Acad. Sci. USSR 112, No. 3, 430 (1957).*

[2] O.P. Golova, A.M. Pakhomov and I.I. Nikolaeva, Bull. Acad. Sci. USSR, div. chem. sci. 1957, 519.*

Received July 5, 1957

N.D. Zelinsky Institute of Organic Chemistry
Academy of Sciences, USSR
Forestry Institute, Acad. Sci. USSR

* Original Russian pagination. See C.B. translation.

LETTERS TO THE EDITOR

ESTIMATION OF THE DISSOCIATION ENERGIES OF C_2H-H AND C_2H_3-H BY THE ION-IMPACT METHOD

The authors' method [1], used previously [2, 1] for the determination of the affinities of H_2O, CH_3OH, and C_2H_5OH for a proton, has now been applied to the estimation of the dissociation energies of the C–H bonds in C_2H_2 and C_2H_4. Investigation on a special mass spectrometer [3] of the results of collisions of $C_2H_2^+$ ions with H_2O molecules and also of CH_3OH^+ ions with C_2H_2 molecules showed that the reactions 1) $C_2H_2^+ + H_2O = H_3O^+ + C_2H + Q_1$ and, 2) $CH_3OH^+ + C_2H_2 = CH_3OH_2^+ + Q_2$ + (Q – heat of reaction), respectively, cannot be detected in the mass spectrometer. Hence, $Q_1 < 0$ and $Q_2 < 0$. Since $J(C_2H_2) = 11.43$ ev, $J(H) = 13.59$ ev, $P_{H_2O} \geq 167$ kcal/mole [1], $J(H_3OH) = 10.95$ ev, and $P_{CH_3OH} > 177$ kcal/mole [2], it follows from Reaction (1) that $D(C_2H-H) > 117$ kcal/mole, and from Reaction (2) that $D(C_2H-H) > 116$ kcal/mole. It was established spectroscopically [4] that $D(C_2H-H) \leq 121$ kcal/mole. We thus find that $D(C_2H-H) = 119 \pm 2$ kcal/mole.* We estimated also the lower limit of possible values of $D(C_2H_3-H)$. In the collision of $C_2H_4^+$ ions with H_2O molecules the reaction 3) $H_2O + C_2H_4^+ = H_3O^+ + C_2H_3 + Q_3$ cannot be detected. Hence, $Q_3 < 0$. Use of the values of $J(C_2H_4) = 10.62$ ev, $J(H)$, and P_{H_2O} leads to the inequality $D(C_2H_3-H) > 97$ kcal/mole.

E.L. Frankevich
and V.L. Talroze

LITERATURE CITED

[1] V.L. Talroze and E.L. Frankevich, Proc. Acad. Sci. USSR No. 2, 376 (1956).

[2] E.L. Frankevich and V.L. Talroze, J. Phys. Chem. (in the press).

[3] E.L. Frankevich and V.L. Talroze, PTE No. 2, 48 (1956).

[4] R. Cherton, Bull. Soc. Sci. Liege 11, 208 (1942).

Received October 7, 1957

Institute of Physical Chemistry
Academy of Sciences, USSR

*The fact that acetylene is not an exception to the rule that exothermal reactions are observable in the mass spectrometer, which lies at the basis of our method, is shown by our detection of the reaction $C_2H_2^+ + NH_3 = C_2H + NH_4^+$.

NEW REACTIONS OF TROPYLIUM SALTS

We have shown that cycloheptatrienylium (tropylium) salts alkylate ("tropylate") compounds containing mobile hydrogen with great ease. Thus, tropylium bromide reacts in the cold with β-keto esters (acetoacetic, ethylacetoacetic, and diacetoacetic esters), β-diketones (acetylacetone, dimedone), and β-dicarboxylic acids and their derivatives (malonic acid, cyanoacetic ester, etc.). Tropylium salts react with various aliphatic aldehydes just as readily. Aliphatic and aliphatic-aromatic ketones also react when heated with tropylium salts. Tropylium salts readily alkylate many aromatic compounds: reaction with resorcinol and phloroglucinol goes in the cold, and reaction with phenol, hydroquinone, and 1- and 2-naphthols go with warming.

Unlike ordinary ethers, tropylium oxide $(C_7H_7)_2O$ alkylates β-keto esters, β-diketones, and β-dicarboxylic acids under very mild conditions. Thus, acetoacetic esters gives cycloheptatrienylacetoacetic ester (b.p. 130° (4 mm); found (%): C 70.95, H 7.34).

Tropylium salts add very readily to compounds containing activated multiple bonds, e.g., to vinyl ethers, cyclopentadiene, phenylacetylene. Thus, reaction of ethyl vinyl ether with tropylium salts gave cycloheptatrienylacetaldehyde (b.p. 62° (2 mm); found (%): C 70.88, H 7.32). Reaction of cyclopentadiene with tropylium bromide in alcohol gave bromocycloheptatrienylcyclopentene (b.p. 113° (3 mm); found (%): C 61.20, H 5.70), and with tropylium perchlorate in water it gave cycloheptatrienylcyclopentenol (b.p. 116° (4 mm); found (%): C 82.61, H 8.06).

The reactions studied reveal new possibilities for the synthesis of cycloheptatriene and tropylium derivatives.

M.E. Volpin, I.S. Akhrem
and D.N. Kursanov

Received October 9, 1957

Institute of Heteroorganic Compounds
Academy of Sciences, USSR

Bulletin of the Academy of Sciences of the USSR

Division of Chemical Sciences

IN ENGLISH TRANSLATION

December, 1957

CONTENTS

	Page	Russ. Page
New Data on the Chemistry of Some of the Rare Elements. I. V. Tananaev	1447	1421
Some General Questions of Electrochemical Kinetics and the Theory of Ionic Reactions. A. N. Frumkin	1454	1429
Nitration of Fluoroolefins with Nitrogen Dioxide. I. L. Knunyants and A. V. Fokin.	1462	1439
Synthesis and Reactions of Vinyl Compounds of Silicon. Communication 3. Preparation of Alkylchlorovinylsilanes by Reaction of Acetylene with Chlorosilanes Containing Silicon-Attached Hydrogen, and Investigation of Some of Their Properties. M. F. Shostakovsky, D. A. Kochkin and V. L. Vinogradov	1474	1452
Investigation of Lactones and Lactams. Communication 9. Synthesis of N-Vinyl Lactams and some of Their Properties. M. F. Shostakovsky, F. P. Sidelkovskaya and M. G. Zelenskaya	1478	1457
Copolymerization of Butadiene with Vinyl Formate. S. N. Ushakov and S. S. Ivanov	1486	1465
Oxide-Metal Catalysts for the Reforming of Gasolines. Communication 2. Reforming of Narrow Gasoline Fractions of Ilsk and Second Baku Petroleums Over Platinum Catalysts. Kh. M. Minachev, N. I. Shuikin, N. F. Kononov, I. L. Garanin and M. A. Ryashentseva	1493	1472
Synthesis of Polyalkylenearyls. Communication 1. Polycondensation of Methylene Chloride with Halobenzenes. G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova	1498	1478
BRIEF COMMUNICATIONS		
Effect of Fine Vibrational Milling on the Activity of Raney Nickel. S. L. Kiperman, A. A. Balandin and I. R. Davydova	1502	1482
1-Naphthyl Compounds of the Type $ArPbX_3$. V. I. Lodochnikova, E. M. Panov and K. A. Kocheshkov	1505	1484
Synthesis of α-Keto Acids Via Azlactones of 2-(Acylamino)-3-Alkyl (or Aryl) Acrylic Acids, and a New Synthesis of 3-Methyl-2-Oxovaleric Acid. Z.S. Kagan.	1508	1486
Telomerization of Propene and Ethylene with Methyl Formate. G. I. Nikishin, V. D. Vorobyev and A. D. Petrov	1511	1488
Cyanoethylation of Methyl- and Ethyl-Dichlorosilanes. A. D. Petrov and V. M. Vdovin	1513	1490
Organomagnesium Synthesis of Vinyl Compounds of Silicon, Germanium and Tin. A. D. Petrov and V. F. Mironov	1516	1491
Relative Efficiencies of Silicon—Copper and Silicon—Nickel Alloys in the Direct Synthesis of Chlorovinylsilanes. M. F. Shostakovsky, E. M. Savitsky, D. A. Kochkin and L. V. Musatova	1519	1493

(continued)

CONTENTS (continued)

	Page	Russ. Page
Products of the Addition of Diazomethane to Unsaturated Compounds. V. V. Korshak and V. A. Sergeev	1522	1495
Free Radical Mechanism of the Thermodegradation of Cellulose and Formation of Levoglucosan. A. M. Pakhomov	1525	1497
Transformations of Cellulose at Elevated Temperatures. Communication 6. Effect of Additions of Glucose on the Formation of Levoglucosan in the Vacuum Thermodegradation of Cellulose. O. P. Golova, A. M. Pakhomov and E. A. Andrievskaya	1528	1499
LETTERS TO THE EDITOR		
Estimation of the Dissociation Energies of C_2H-H and C_2H_3-H by the Ion-Impact Method. E. L. Frankevich and V. L. Talroze	1529	1501
New Reactions of Tropylium Salts. M. E. Volpin, I. S. Akhrem and D. N. Kursanov	1530	1501

NUCLEAR REACTIONS IN LIGHT NUCLEI
IN ENGLISH TRANSLATION

Supplement No. 5, 1957 Soviet Journal of Atomic Energy

Ten papers describing in detail (with diagrams of all apparatus), important experiments by the Academy of Sciences, USSR, 1951–1955. Mainly concerned with measurements of the total and differential cross sections and product angular distributions in interactions involving isotopes of light elements, many of which are of interest in connection with thermonuclear fusion reactions. Makes detailed comparisons of all available experimental data; discusses errors and means of avoiding them; refers extensively to Soviet and non-Soviet literature.

CONTENTS: Determination of the total cross sections for the $D(d,n)He^3$ reaction in the energy range 20–220 kev; Investigation of the D-D reaction in the deuteron-energy range 0.20–1.75 Mev; The D-D reaction in the deuteron-energy range 100–1000 kev; Measurements of the yields and effective cross sections of the $D(t,n)He^4$ and $D(d,p)T$ reactions using thick targets of heavy ice; Measurement of the effective cross section for the $D(t,n)He^4$ reaction in the deuteron-energy range 40–730 kev; Total effective cross section of tritium for neutrons with energies of 2.5 and 14 Mev; Measurement of the effective cross section for the Li^6 (n,d) reaction for 2.5 Mev neutrons; Total effective cross sections for Li^6 and Li^7 for neutrons with energies of 2.5 and 14 Mev; Effective cross section for the $Be^9(n,d)He^6$ reaction; Specific stopping power of 150–1100 Mev in nickel. English translation, 71 pages, $15.00

***For subscribers to our translation of the 1957 Soviet Journal of Atomic Energy only $10.00**

* * * *

ACOUSTICS AND ULTRASONICS
RUSSIAN-ENGLISH GLOSSARY

10,000 Russian terms. Covers acoustics, ultrasonics electro-acoustics, with emphasis on the rapidly growing field of ultrasonics. Terms selected from thousands of pages of the most recent issues of Soviet physics and engineering journals, especially the Journal of Acoustics, the Journal of Technical Physics, and Radio-Engineering, as well as from Russian acoustics texts. Russian equivalents are also provided for terms selected from the following: IRE Standards; the International Dictionary of Physics and Electronics; the Russian translation of L. Bergman's "Ultrasonics Theory". 23 page index of Russian-English equivalents for names commonly found in acoustics and ultrasonics literature. 193 pages, only $10.00

This is the latest in a series of 8 specialized glossaries being published preliminary to publication, in 1959, of our Russian-English Physics Dictionary, which will be comprehensive, authoritative, permanently bound. *Pre-publication subscribers to the Dictionary* also receive each of the 8 glossaries upon publication **all for only $50.00**

Write for free catalogs fully describing the Dictionary and 8 glossaries, as well as our current Russian-English translation-publishing program.

Consultants Bureau's translation by *bilingual scientists*. Clear reproduction by multilith process from IBM "cold type", (except glossaries, which are varityped), including all diagrammatic and tabular material; books staple bound in durable paper covers.

CONSULTANTS BUREAU, INC.

227 WEST 17th STREET, NEW YORK 11, N.Y.

Telephone: ALgonquin 5-0713 • Cable Address: CONBUREAU, NEW YORK

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE

BETHESDA 14, MD.

NATIONAL INSTITUTES OF HEALTH

August 15, 1958

Mr. Earl Coleman
Consultants Bureau
227 West 17th Street
New York 11, New York

Dear Earl:

Now that we are about to renew our contract for another year for translated issues of Biochemistry and Bulletin of Experimental Biology and Medicine, it seems appropriate to review the performance of Consultants Bureau over the past year. This is even more pertinent because the circumstances under which we procure these translations from your firm differs from those under which we contract for the publication of other journals. Since these two translated journals were started at your initiative, and are the property of Consultants Bureau, your firm has complete independence in the matter of translation quality and speed of publication.

In distributing these two journals to 400 medical research libraries we have exposed them to the white light of publicity before a highly critical scientific community. We have yet to receive a single letter critical of the translations made by your firm. To the contrary, we have been receiving a number of letters from medical scientists, and their spokesmen, the medical libraries, throughout the country, reporting how highly thought of these journals are in the scientific community. This speaks volumes for the high standards of translation and editing which you have established and maintained.

We are equally pleased with the speed of delivery of these translated journals. I am well aware of the tremendous strains on your production staff occasioned by the sharp accumulations of pressures for the translation of Russian science and technology. The fact that your staff has been able to maintain its translation and publication schedules, and produce these and the other journals on your program without interruption during these critical months is indeed a cause for congratulations.

On our part, we are gratified both with your product, and with the contribution it has made to the advancement of medical research in the United States. We are placing this renewal order with you in full confidence that the future issues of these two translated journals will maintain the high standards you have set for yourself.

Sincerely yours,

Scott Adams

Scott Adams, Librarian
National Institutes of Health